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FUNDAMENTAL STUDIES ON REACTIVE OLIGOMERS

G. F. D'ALELIO

UNIVERSITY OF NOTRE DAME

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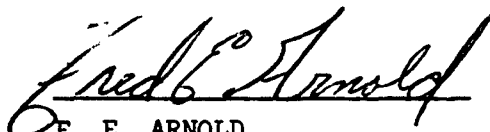
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The final report was submitted by the Department of Chemistry at the University of Notre Dame, Notre Dame, Indiana, under contract F33615-72-C-1312, job order 734201, with the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Dr. F. E. Arnold, MBP was the laboratory project monitor.

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This technical report has been reviewed and is approved for publication.

F. E. ARNOLD
Project Monitor

FOR THE COMMANDER

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Bis[4-(3-acetamidophenoxy)phenyl] Sulfone; Bis[4,(3-aminophenoxy)phenyl] Sulfone; Epoxy-Terminated Oligomeric Polyimides; Styrene-Terminated Oligomeric Polyimides; Styrene-Oxide-Terminated Oligomeric Polyimides; Phthalonitrile-Terminated Oligomeric Polyimides; Thermally-Stable Polyimides; Thermally-Stable Polymers; End-Capped Polyimides; Chain-Extension of End-Capped Polyimides; (continued)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research reported in AFML-TR-73-65, February 1973 was continued. A new aromatic diamine, bis[4-(3-aminophenoxy)phenyl] sulfone (BAPS-4,3) was prepared by hydrolysis of the precursor, bis[4-(3-acetamidophenoxy)phenyl] sulfone, whereas attempts to prepare the nitro-precursor of BAPS-4,3 from the chlorophenyl sulfone and sodium nitrophenoxide were unsuccessful. 4-Aminophthalonitrile was prepared in high purity by the catalytic reduction of 4-nitrophthalonitrile.

A number of epoxide-terminated oligomeric aromatic polyimides (continued)

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Block 19. (continued) (Keywords)

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Block 20. (continued) (Abstract)

(BTEP series) were synthesized by the simple, direct reaction of amine-terminated oligomeric polyimides with epichlorohydrin in the presence of base. They were converted to cured products by heating, alone, or in the presence of curing agents. A number of cured products showed TGA inflection points in air in the 450-490°C region. The peroxidation of a styrene-terminated oligomer yielded an epoxide-terminated oligomer (BTSO series) whose TGA value in air showed a break in the 350-400°C region, and inflection points in the 565-595°C region.

A phthalonitrile-terminated oligomer (BTPN-1) was prepared using 4-aminophthalonitrile as the telomerizing fraction. BTPN-1 was chain-extended by heating alone or with copper compounds. The copper compounds reacted with BTPN-1 apparently to form phthalocyanine bridges. The TGA values in air for the cured products were in the 475-485°C region. A styrene end-capped oligomeric polyimide, BTAS-16, based on the new siamine, BAPS-3, when cured, showed a TGA inflection point in air in the 475°C region.

A new polyimide, PI-25, based on BAPS-4,3, was prepared and its tractability and thermal behavior were similar to polyimides PI-17 and PI-20 based on 1,3-di(4-aminophenoxy)benzene (DAPB-3,3).

SUMMARY

The research reported in AFML-TR-73-65, February 1973 was con-
tinued. A new aromatic diamine, bis[4-(3-aminophenoxy)phenyl]
sulfone (BAPS-4,3) was prepared by hydrolysis of the precursor,
bis[4-(3-acetamidophenoxy)phenyl] sulfone, whereas attempts to pre-
pare the nitro-precursor of BAPS-4,3 from the chlorophenyl sulfone
and sodium nitrophenoxide were unsuccessful. 4-Aminophthalonitrile
was prepared in high purity by the catalytic reduction of 4-nitro-
phthalonitrile.

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and PI-20 based on 1,3-di(4-aminophenoxy)benzene (DAPB-3,3).

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SECTION I

INTRODUCTION

The objective of this research project was the synthesis and character-
ization of tractable reactive oligomers which could be converted to thermally
stable, high molecular weight polymers with a minimum of by-product elimina-
tion and low-to-moderate condensation and post-curing temperatures.

This research is a continuation of the effort reported in AFML-TR-33-65,
February 1973.

One of the objectives of this study was to prepare completely cyclized
oligomeric polyimides having epoxy groups as termini on the chain which
would be more tractable than the previously prepared epoxy derivatives [1].

A second objective was to prepare completely cyclized phthalonitrile-
terminated oligomeric polyimides which, by chain extending reactions, would
yield metal-phthalocyanine linkages; such linkages would be expected to have
higher thermal stability than the bonds resulting from the chain extension
of the styrene-end-capped oligomeric polyimides.

Another objective was to improve further the tractability of the poly-
imides over those based on 1,3-di(3-aminophenoxy)benzene, (DAPB-3,3). To
this end, the synthesis of an aromatic diamine having both ether and sulfone
linkages, such as $H_2NC_6H_4OC_6H_4SO_2C_6H_4OC_6H_4NH_2$, was undertaken to be evalu-
ated in the syntheses of a linear non-telomerized polyimide and of a styrene-
end-capped oligomeric polyimide.

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EXPERIMENTAL

A. Preparation of Intermediates.

1. Preparation of 1,3-Di(4-nitrophenoxy)benzene (DNPB-3,4).

The procedure previously reported [2] was repeated to prepare DNPB-3,4 as the precursor of DAPB-3,4.

2. Preparation of 1,3-Di(4-aminophenoxy)benzene (DAPB-3,4).

The procedure previously reported [3] was repeated to prepare DAPB-3,4 for use in epoxidation studies and for the preparation of polyimides.

3. Attempted Preparation of Bis[4-(4-nitrophenoxy)phenyl] Sulfone (BNPS-4,4). Reaction of 4-Chlorophenyl Sulfone and Sodium p-Nitrophenoxide.

In a 100-ml round-bottom flask equipped with a magnetic stirrer and a condenser was placed a solution of 4-chlorophenyl sulfone (5.7434 g, 0.002 mole) in a 50 ml of methyl ethyl ketone. Then sodium p-nitrophenoxide (17.899 g, 0.1 mole) was added and the mixture was heated to reflux. After 8 hours of reflux, the solution was cooled and then added to water. A white precipitate formed which was filtered off, washed well with water and dried to give white crystals of 4-chlorophenyl sulfone (5.5 g), m.p. 145-149°C.

4. Attempted Preparation of Bis[4-(4-nitrophenoxy)phenyl] Sulfone (BNPS-4,4). Reaction of 4-Chlorophenyl Sulfone and Sodium p-Nitrophenoxide.

In a 200-ml round-bottom flask equipped with a magnetic stirrer and a condenser was placed sodium p-nitrophenoxide (17.899 g, 0.1 mole), 4-chloro-phenylsulfone (5.7484 g, 0.02 mole) and 100 ml of diglyme. The mixture was heated to reflux. Reflux was continued for 165 hours, during which time the solution acquired a golden color. After cooling, the mixture was added to 750 ml of water. A precipitate formed which was filtered off, washed well with water and vacuum-dried, to give a brown solid (5.9204 g, 60%), m.p. 120-127°C. Recrystallization from acetic acid-water afforded 3.4760 g (35%) of a tan solid, m.p. 133-136°C. A small sample was recrystallized a second time from acetic acid-water to afford tan crystals, m.p. 140-162°C, DTA m.p. 141°C (corr.). A sample of the twice-recrystallized material was submitted for analysis.

Analysis: Calc'd for $C_{24}H_{16}N_2O_8S$ (BNPS-4,4)

C, 58.52; H, 3.28; N, 5.69; O, 25.99; S, 6.51.

Calc'd for $C_{12}H_8Cl_2O_2S$ (4-chlorophenylsulfone)

C, 50.11; H, 2.81; Cl, 24.67; O, 11.18; S, 11.20.

Found: C, 50.91; H, 3.09; N,   0.5.

5. Attempted Preparation of Bis[4-(3-nitrophenoxy)phenyl] Sulfone (BNPS-4,3). Reaction of 4,4'-Sulfonyldiphenol with 1,3-Bromonitrobenzene.

In a 300-ml round-bottom flask equipped with a magnetic stirrer and distillation head was placed 4,4'-sulfonyldiphenol (12.514 g, 0.5 mole) and sodium methoxide (5.401 g, 0.1 mole) in 100 ml of diglyme. The mixture was heated until approximately 5 ml of diglyme distilled over. After cooling, 1,3-bromonitrobenzene (40.4 g, 0.2 mole) was added and a reflux condenser was installed in place of the distillation head. The mixture was heated and stirred at reflux for 24 hours and then cooled. The mixture was added to 200 ml of water, acidified with 2% hydrochloric acid and extracted with benzene. Upon addition of the benzene, a white solid precipitate formed, which was filtered off, washed with benzene and vacuum-dried to give 10.0623 g of a white solid which melted at 245-248°C. It was shown by its infrared spectrum to be unreacted 4,4'-sulfonyldiphenol (80% recovery).

6. Attempted Preparation of Bis[4-(3-nitrophenoxy)phenol] Sulfone (BNPS-4,3). Reaction of 4,4'-Sulfonyldiphenol with 1,3-Bromonitrobenzene.

The procedure reported above in A.5 was repeated using 4,4'-sulfonyldiphenol (5.0054 g, 0.02 mole), sodium methoxide (2.1604 g, 0.04 mole), 1,3-bromonitrobenzene (20.2 g, 0.1 mole) and cuprous chloride (0.1 g) in 30 ml of diglyme. After refluxing for 20 hours, the mixture was cooled and treated as in A.5 to give 4,4'-sulfonyldiphenol in a 92% recovery. A 90% recovery of the 1,3-bromonitrobenzene was obtained from the benzene layer.

7. Attempted Preparation of Bis[4-(4-nitrophenoxy)-phenyl] Sulfone (BNPS-4,4). Reaction of 4-Chloro-phenyl Sulfone with Sodium p-Nitrophenoxide.

Into a 250-ml three-neck, round-bottom flask equipped with a magnetic stirrer, dropping funnel, thermometer and distillation head was placed 4-nitrophenol (27.822 g, 0.2 mole), 45 g of DMSO, and 125 g of chlorobenzene. The mixture was stirred, forming a clear solution. A slow stream of nitrogen was passed through the solution and sodium hydroxide (8.00 g, 0.2 mole) in 10 ml of water was added. Heating was begun and a chlorobenzene-water azeotrope was distilled off. When the reaction temperature reached 160°C, a solution of 4-chlorophenyl sulfone (28.717 g, 0.1 mole) in 100 ml of chlorobenzene was added. Heating and stirring were continued with removal of chlorobenzene for 2 hours. Then the reaction temperature was raised to 190°C and maintained at that temperature for 2 hours. After cooling, the reaction mixture was slowly added to approximately 1 Kg of ice water. A tarry residue

formed, which was washed two times with water. All attempts to isolate crystalline material from the tar failed and the work-up was discontinued.

8. Preparation of 4-Hydroxyacetanilide. Reaction of 4-Aminophenol with Acetic Anhydride.

According to a published procedure [4], 4-aminophenol (11.0 g) was allowed to react with acetic anhydride (12 ml) in 30 ml of water. After one recrystallization from water there was obtained 12.2 g of white crystals, m.p. 169°C (lit. m.p. [4], 168°C).

9. Preparation of 3-Hydroxyacetanilide. Reaction of 3-Aminophenol with Acetic Anhydride.

According to the procedure reported above [4] there was allowed to react 3-aminophenol (11.0 g) with acetic anhydride (12 ml) in 30 ml of water. After one recrystallization from water there was obtained 12.0 g of white crystals, m.p. 148-149°C (lit. m.p. [5], 149°C).

10. Attempted Preparation of Bis[4-(4-acetamidophenoxy)-phenyl] Sulfone (BACS-4,4). Reaction of 4-Chlorophenyl Sulfone with the Sodium Salt of 4-Hydroxyacetanilide.

In a 300-ml three-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, distillation head and nitrogen inlet was placed 4-hydroxyacetanilide (7.558 g, 0.05 mole), 75 ml of diglyme, 50 ml of pyridine and sodium methoxide (2.700 g, 0.05 mole). The mixture was heated to 100°C under nitrogen and methanol was distilled off. The mixture was cooled and 4-chlorophenyl sulfone (7.180 g, 0.025 mole) was added. The distillation head was removed and a reflux condenser inserted in its place. The mixture was heated at reflux (135-140°C) for 6 hours and then allowed to cool. Then the mixture was added to approximately 1 Kg of ice-water. A white solid formed, which was filtered off, washed well with water and vacuum-dried at 50°C to afford 7.031 g of unreacted 4-chlorophenyl sulfone, identified by its melting point (145-147°C) and infrared spectrum, which was identical to the infrared spectrum of the starting material (Figure 1).

11. Attempted Preparation of Bis[4-(3-acetamido-phenoxy)phenyl] Sulfone (BACS-4,3). Reaction of the Sodium Salt of 3-Hydroxyacetanilide with 4-Chlorophenyl Sulfone in DMF.

In a 250-ml two-neck, round-bottom flask equipped with a magnetic stirrer, nitrogen inlet and distillation head, was placed 7.558 g of 3-hydroxyacetanilide (0.05 mole) and 2.700 g (0.05 mole) of sodium methoxide in 60 ml of DMF. A slow stream of nitrogen was passed through the mixture, then heating and stirring were begun. Methanol was distilled off until the temperature at the distillation head reached 100°C. The resulting slurry was cooled and 4-chlorophenyl sulfone (7.180 g, 0.025 mole) was added. The mixture was heated to reflux and maintained at the reflux temperature for 22 hours. During the reflux period, the yellow color gradually faded. The mixture was then cooled and added to 500 g of ice-water, yielding an off-white oily material. The oil was digested in hot water and then the water was decanted. The wash procedure was repeated three times and then the oil

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was vacuum-dried at 90°C for 24 hours, to yield an extremely sticky solid. The sticky solid was recrystallized twice from glacial acetic acid to afford white crystals (2.112 g, 17.5%), m.p. 145-148°C. The infrared spectrum displayed bands at 2.95μ, 6.08μ, 7.52μ, 8.60μ, 7.80μ and 9.85μ, which were substantially identical to the bands for 4-chlorophenylsulfone of Figure 1.

12. Attempted Preparation of Bis[4-(3-acetamido-phenoxy)phenyl] Sulfone (BACS-4,3). Reaction of 4-Chlorophenyl Sulfone with 3-Hydroxy-acetanilide in Pyridine.

Into a 300-ml three-neck, round-bottom flask equipped with a distillation head, nitrogen inlet and magnetic stirrer was placed 3-hydroxyacetanilide (30.232 g, 0.20 mole), sodium methoxide (10.800 g, 0.20 mole) and 250 ml of pyridine. The mixture was heated and stirred under nitrogen until the temperature at the distillation head reached 100°C. After cooling, 4-chlorophenyl sulfone (28.717 g, 0.10 mole) and 5.1 g of cuprous chloride were added. A reflux condenser was inserted in place of the distillation head. The mixture was heated and stirred at reflux for 24 hours, during which time the mixture darkened considerably. After cooling, 100 ml of water and 300 ml of benzene were added. The mixture was made slightly acidic with concentrated hydrochloric acid. The benzene layer was separated. The aqueous layer was extracted three times with 200 ml of benzene. The benzene fractions were combined, washed three times with 100 ml of water and dried over anhydrous sodium sulfate. The benzene was removed on a rotary flash evaporator, leaving an off-white solid, 28.103 g (98% recovery) after vacuum-drying at 40°C for 24 hours. The melting point was 100-130°C; the infrared spectrum was virtually identical with that of 4-chlorophenyl sulfone.

13. Preparation of Bis[4-(3-aminophenoxy)phenyl] Sulfone (BAPS-4,3). Reaction of 4-Chlorophenyl Sulfone with 3-Hydrodyacetanilide in DMF, Followed by Hydrolysis.

Into a 300-ml three-neck, round-bottom flask equipped with a distillation head, a nitrogen inlet and a magnetic stirrer was placed 3-hydroxyacetanilide (30.232 g, 0.20 mole), sodium methoxide (10.800 g, 0.20 mole) and 200 ml of DMF. The mixture was heated and stirred under nitrogen until the temperature at the distillation head reached 100°C. After cooling, 4-chlorophenyl sulfone (28.717 g, 0.10 mole) and 1.1 g of cuprous chloride were added. Then, a reflux condenser was inserted in place of the distillation head. The mixture was heated at reflux and stirred for 48 hours, during which time the mixture darkened considerably. The mixture was cooled, concentrated on a rotary flash evaporator and added to 1 liter of water, yielding a light-brown colored oil. The water was decanted and fresh water (1 liter) was added. The mixture was heated to boiling briefly, cooled and the water decanted. This washing procedure was repeated three times. The brown oil was dissolved in 500 ml of hot 95% ethanol, filtered and the filtrate was flash-evaporated to yield a brown solid, 13.096 g; m.p., after vacuum-drying at 50°C for 48 hours, 70-77°C. The infrared spectrum (KBr disc, Figure 2) displayed bands at 2.95μ and 5.98μ, for the secondary amide function, as well as bands at 8.63μ and 7.57μ for the sulfone group. This material was very soluble in ethanol, chloroform and THF; but was insoluble in benzene and water.

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A sample (9.246 g) of this bis[4-(3-acetamidophenoxy)phenyl] sulfone was refluxed for 20 hours in 125 ml of concentrated hydrochloric acid. After cooling, the mixture was evaporated on a rotary flash evaporator and then vacuum-dried at 50°C for 20 hours to afford 9.154 g (approximately 100%) of a red, glassy mass.

A sample (8.000 g) of the hydrochloride salt from above was dissolved in 50 ml of water. Then 200 ml of 10% of sodium hydroxide was added, with stirring, to the mixture. The mixture was extracted five times with 100 ml of warm benzene. The benzene layers were combined, washed once with water, dried (sodium sulfate) and evaporated on a rotary flash evaporator. After vacuum-drying at 30°C for 20 hours, there was obtained 6.350 g (93%) of a red glass. A thin layer chromatogram (silica gel; developed with benzene) showed several bands. Accordingly, the material was chromatographed through a 8" x 1" column, using silica gel and eluting with 200 ml each of benzene, 10% ethanol in benzene, 20% ethanol in benzene, 30% ethanol in benzene, 100 ml of 50% ethanol in benzene and 200 ml of absolute ethanol. Eight fractions of 125-150 ml were collected. The fractions were evaporated and vacuum-dried to yield: I, 2.989 g of a white solid; II, 0.809 g of a white solid; III, 2.234 g of a red glass, and IV to VIII, 0.0053 g of a dark residue. The infrared spectra of fractions I and II were similar, while that of fraction III was noticeably different from those of fractions I and II. All three showed absorption for the amine function. Fractions I and II were combined as Sample A and recrystallized from benzene-cyclohexane to afford 1.804 g of a white powder, m.p. 132-178°C.

Fraction III was labelled as Sample B; it melted over the range 65-75°C; its infrared spectrum is given as Figure 3.

Analysis: Calc'd for $C_{24}H_{20}N_2O_4S$ (BAPS-4,3)

  C, 66.65; H, 4.66; N, 6.47; O, 14.79; S, 7.41.

Calc'd for $C_{24}H_{22}Cl_2N_2O_4S$ (BAPS-4,3-di.HCl)

  C, 57.03; H, 4.39; N, 5.54; O, 12.66; S, 6.34; Cl, 14.03.

Found (Sample A):

  C, 62.52; H, 4.63; N, 5.44; O, -----; S, ----.

Found (Sample B):

  C, 66.80; H, 5.05; N, 6.13; O, -----; S, ----.

14. Preparation of Bis[4-(3-aminophenoxy)phenyl] Sulfone (BAPS-4,3). Reaction of 4-Chlorophenyl Sulfone with 3-Hydroxyacetanilide in DMF, Followed by Hydrolysis.

The reaction described under A.13 was repeated using twice the quantities of reactants and increasing the amount of cuprous chloride to 5.0 g, and there was obtained 94.6 g (91.5%) of a red, glassh product.

A 50.00 g sample of the red, glassy product was refluxed for 24 hours in 700 ml of concentrated hydrochloric acid. After cooling, the reaction mixture was concentrated to approximately one-half the original volume on a rotary flash evaporator. Concentrated hydrochloric acid (200 ml) and absolute ethanol (200 ml) were added and the mixture was refluxed for 24 hours. After cooling, the mixture was evaporated on a rotary flash evaporator. The residue was treated with 10% aqueous NaOH until the liquor was definitely basic, and then flash evaporated to dryness. The residue was digested twice with hot benzene, and the benzene solutions were filtered. The benzene was removed on a rotary flash evaporator and the residue was vacuum-dried at 40°C for 24 hours, to give 37.3 g of a red, glassy material.

The glassy material displayed several bands on a thin layer chromatographic (TLC) plate developed with benzene. Accordingly, it was chromatographed on a 8" x 1" silica gel column. The column was eluted with 1500 ml of benzene, 200 ml of 5% ethanol-benzene, 600 ml of 10% ethanol-benzene, 200 ml of 20% ethanol-benzene, 100 ml of 50% ethanol and 200 ml of absolute ethanol respectively. Fractions of 100-200 ml were collected. The second fraction, after flash evaporation, yielded 32.189 g of a yellow, glassy material which gave two bands on a TLC plate developed with benzene. This material was dissolved in 100 ml of benzene and chromatographed in two 50-ml portions on a 8" x 1" silica gel column eluted with 400 ml of benzene, 200 ml of 10% ether-benzene, 400 ml of 25% ether-benzene and 200 ml of 10% ethanol-benzene respectively. Eight fractions of approximately 100 ml were collected.

The third through the eighth fractions gave, after flash evaporation and vacuum-drying, materials which were identical with BAPS-4,3 previously prepared under A.13, in their infrared spectra (Figure 3) and in their TLC values when developed with benzene.

The final total yield was 6.577 g (14% from the diacetamido compound, BACS-4,3) of an off-white solid, m.p. 65-80°C, with most of the material melting at 78-80°C. A small sample was recrystallized from benzene and submitted for elemental analysis, m.p. 79-81°C.

Analysis: Calc'd for $C_{24}H_{20}N_2O_4S$ (BAPS-4,3)

C, 66.65; H, 4.66; N, 6.47; O, 14.79; S, 7.41.

Found: C, 66.53; H, 4.82; N, 6.54; O, -----; S, ----.

15. Preparation of 4-Nitrophthalamide (NPA). Reaction of 4-Nitrophthalimide (NPI) and Aqueous Ammonium Hydroxide.

Into an Erlenmeyer flask was placed 9.1 g of NPI and 75 ml of concentrated aqueous ammonium hydroxide. The slurry was stirred at ambient temperature for 3 hours. Then, the solid was filtered off, washed well with water and vacuum-dried at 40°C for 2 days to afford NPA, 8.7 g (88%), as a tan solid, m.p. 198-199°C (lit. m.p. [6], 194-5-195°C). The infrared spectrum of NPA is given in Figure 4.

16. Preparation of 4-Nitrophthalamide (NPA). Reaction of 4-Nitrophthalimide (NPI) and Aqueous Ammonium Hydroxide.

According to the procedure reported above, NPI (25.0 g) and ammonium hydroxide (200 ml) were allowed to react for 4 hours. There was obtained NPA (22.0 g, 81.5%), m.p. 198-199°C (lit. m.p. [6], 194.5-195°C).

17. Preparation of 4-Nitrophthalonitrile (NPN). Reaction of 4-Nitrophthalamide (NPA) with Thionyl Chloride.

In a 50-ml Erlenmeyer flask equipped with a magnetic stirrer, was placed NPA (4.183 g, 0.02 mole) and 25 ml of DMF. The mixture was stirred in an ice bath for 15 minutes. Solution of the NPA did not occur. Then thionyl chloride (10 ml) was added to the slurry. The NPA dissolved immediately, forming an orange-colored solution. After continued stirring on the ice bath for 15 minutes, the ice bath was removed, and stirring was continued for 18 hours at ambient temperature. The solution was then added to 150 ml of water, stirred for 15 minutes and filtered. The solid thus obtained was washed well with water and then vacuum-dried at 40°C for 24 hours to give NPN, 1.8530 g (53.5%) as a tan solid, m.p. 131-134°C (dec.). A sample was recrystallized from ethanol to afford tan crystals, m.p. 136-138°C (dec.) (lit. m.p. [7], 142°C). The infrared spectrum is given in Figure 5.

18. Preparation of 4-Nitrophthalonitrile (NPN). Reaction of 4-Nitrophthalamide (NPA) with Thionyl Chloride.

Into a 100-ml Erlenmeyer flask equipped with a magnetic stirrer was placed thionyl chloride (25 ml) and DMF (25 ml). The mixture was cooled and stirred on an ice bath for 15 minutes and then NPA (10.0 g) was added. Then an additional 25 ml portion of thionyl chloride was added. After stirring on the ice bath for 5 minutes, the ice bath was removed. Complete solution of the NPA occurred 10 minutes after the addition of the NPA. Stirring was continued for a total of 30 minutes. The clear orange-colored solution was added slowly to 400 g of ice. The mixture was stirred until the ice melted, and then filtered. The solid thus obtained was washed well with water and vacuum-dried at 40°C for 24 hours to afford NPN (5.1 g, 61.5%) as a tan solid, m.p. 139-140°C (lit. m.p. [7], 142°C).

19. Preparation of 4-Nitrophthalonitrile (NPN). Reaction of 4-Nitrophthalamide (NPA) with Thionyl Chloride.

In a 200-ml round-bottom, three-neck flask equipped with a magnetic stirrer, thermometer and condenser was placed 50 ml of thionyl chloride. The flask was placed into an ice bath and then 50 ml of DMF was added at a rate such that the temperature was maintained below 20°C. When the addition was complete the mixture was cooled to 10°C and then NPA (20.0 g) was added. The temperature of the mixture rose to 20°C and then began to fall. After stirring for 10 minutes, the ice bath was removed and stirring was continued for 1 hour. The clear, orange-colored solution was then added, with stirring, to 200 g of ice. Stirring was continued until the ice melted and the solid thus obtained was filtered off, washed well with water and vacuum-dried to give NPN (12.0 g, 73%) as a tan solid, m.p. 141-142.5°C (lit. m.p. [7], 142°C).

20. Preparation of 4-Aminophthalonitrile (APN).
Reaction of 4-Nitrophthalonitrile (NPN) with
Sodium Hydrosulfite (Na$_2$S$_2$O$_4$).

Into a 100-ml Erlenmeyer flask, equipped with a magnetic stirrer and a
thermometer, was placed sodium hydrosulfite (17.4 g, 0.1 mole) and NaOH
(4.00 g, 0.1 mole) in 75 ml of water. Then NPN (4.33 g, 0.025 mole) was
added portionwise over approximately 15 minutes so that the temperature was
maintained at 40-50°C. During the addition of the NPN, the color of the
solution changed from water-white to red, then to orange and finally to
yellow; a copious precipitate was present when the addition was complete.
Stirring was continued for an additional 15 minutes. Then the solution was
filtered and the solid thus obtained was washed well with water. It was
then taken up into 100 ml of warm ethanol, filtered and the ethanolic solu-
tion was evaporated on a rotary flash evaporator. The residue was vacuum-
dried at 40°C for 18 hours to afford a tan solid, APN, 1.278 g (35.6%, m.p.
dec. 151-160°C (lit. m.p. [7] dec., 160-170°C). The infrared spectrum, given
as Figure 6, displays bands at approximately 3μ for -NH$_2$ and at approximately
4.5μ for -C≡N. The aqueous filtrate obtained above was extracted three times
with 100 ml of ether, the organic layer was dried over Na$_2$SO$_4$ and then evapo-
rated on a rotary flash evaporator. The residue was vacuum-dried at 40°C
for 18 hours to afford a bright yellow solid, 1.232 g, whose infrared spec-
trum displayed bands at approximately 3μ for -NH$_2$, 4.5μ for -C≡N, and at
4.68μ and 5.84μ, probably for -COOH.

21. Attempted Preparation of 4-Aminophthalonitrile (APN).
Catalytic Reduction of 4-Nitrophthalonitrile (NPN).

In a 300-ml high-pressure catalytic hydrogenation vessel was placed
18.5 g of NPN, 0.50 g of 5% palladium-on-charcoal, and 120 ml of absolute
ethanol. The vessel was charged with hydrogen to a pressure of 600 psi.
The vessel was rocked at ambient temperature for 4 hours and then at 37°C
for 1 hour, at which time the take-up of hydrogen ceased. The vessel was
cooled and the solution was filtered through a celite-coated paper. The
filtered solution was evaporated on a rotary flash evaporator to yield a
yellow solid which was vacuum-dried at ambient temperature for 24 hours, to
yield a cream-colored solid, 13.187 g (86%), m.p. 112-120°C (dec.). The
infrared spectrum of the solid displayed bands at 2.89 and 3.00 for -NH$_2$,
at 4.50μ for -CN, and at 6.50μ and 7.40μ for NO$_2$. An attempted recrystalli-
zation from ethanol-water gave a material whose infrared spectrum still
contained bands for both the amino and the nitro groups.

22. Preparation of 4-Aminophthalonitrile (APN).
Catalytic Reduction of 4-Nitrophthalonitrile (NPN).

A 300-ml, high-pressure reaction vessel was charged with 4-nitrophthalo-
nitrile (15.0 g), 5% palladium-on-charcoal (1.0 g) and 125 ml of absolute
ethanol. The initial hydrogen pressure was 700 psi and the vessel was rocked
at ambient temperature for 2 hours, and then at 50°C for 3 hours, by which
time hydrogen take-up had ceased. The pressure drop was approximately two-
thirds of the theoretical pressure drop. The vessel was opened, the cata-
lyst filtered off and the filtrate was concentrated on a rotary flash evapo-
rator. The reaction vessel was recharged with the concentrate, fresh 5%

palladium-on-charcoal (1.0 g) and ethanol to make a total volume of 125 ml.
The vessel was charged with hydrogen to 600 psi and rocked at 50°C for 6
hours. After cooling, the vessel was opened and the catalyst was filtered
off. The filtrate was evaporated to yield a brown solid, 9.7 g (88%); m.p.
decomposes above 160°C, melts at 173-176°C (lit. m.p. [6], 160-170°C).

A small sample was recrystallized from water to afford yellow crystals,
m.p. 181-183°C, whose infrared spectrum is given as Figure 7. A small sample,
when treated with acetic anhydride, gave yellow crystals of the acetamide,
m.p. 196-198°C (lit. m.p. [6], 194°C).

B. Oligomers.

1. Preparation of Amine-Terminated Oligomeric Polyimide (BTAT-6). Reaction of BTCA and DAPB-3,3 (4:5).

The procedure previously reported [8] was used to prepare BTAT-6.

2. Preparation of Styrene-Terminated Oligomeric Polyimide (BTAS-12). Reaction of BTCA, DAPB-3,3 and AS (5:4:2).

The procedure previously reported [9] was used to prepare BTAS-12 for
epoxidation studies.

3. Preparation of Phthalonitrile-Terminated Oligomeric Polyimide (BTPN-1). Reaction of BTCA, SDA-3,3 and APN (5:4:2).

According to the m-cresol:azeotropic technique [8] there was allowed
to react BTCA (3.2223 g, 0.01 mole), SDA-3,3 (1.9865 g, 0.008 mole) and APN
(0.5726 g, 0.004 mole) in 40 ml of m-cresol and 10 ml of benzene.

After the usual isolation procedure there was obtained 4.9825 g (90.5%)
of a yellow powder (BTPN-1) whose infrared spectrum is given as Figure 8.
The TGA in air displayed an inflection point in excess of 550°C. On a
Fisher-Johns melting point apparatus BTPN-1 melted over the range 255-285°C
and did not harden in 10 minutes at 300°C. BTPN-1 was soluble in m-cresol,
DMAC and sulfolane. Its TGA in air is given in Figure 9. A sample was
submitted for analysis.

Analysis: Calc'd for $C_{149}H_{68}N_{14}O_{33}S_4$

C, 66.03; H, 2.46; N, 7.24; O, 19.49; S, 4.74.

Found: C, 66.99; H, 2.66; N, 6.87; O, -----; S, ----.

4. Preparation of Styrene-Terminated Oligomeric Polyimide (BTAS-16). Reaction of BTCA, BAPS-4,3 and AS (5:4:2).

A procedure previously reported [9] for the preparation of BTAS-type
oligomers was used to react BTCA (1.611 g, 0.005 mole), BAPS-4,3 (1.7299 g,
0.004 mole, Sample B of A.13) and AS (0.2383 g, 0.002 mole) to afford 3.07 g

(90.3%) of BTAS-16. Its infrared spectrum is given in Figure 10 and the TGA in air is given in Figure 11.

Analysis: Calc'd for $C_{197}H_{108}N_{10}O_{41}S_4$

C, 69.40; H, 3.20; N, 4.11; O, 19.31; S, 3.78.

Found: C, 68.87; H, 3.39; N, 3.76; O, -----; S, ----.

C. Polymers.

1. Epoxy Systems.

a. Preparation of Epoxy Resins.

i. Preparation of Epoxy Resin (EP-1). Reaction of ODA with EPC in the Presence of NaOH (2 moles) for 24 Hours.

A mixture of ODA (5.0060 g, 0.025 mole), EPC (50 ml) and NaOH (2.00 g, 0.05 mole) was heated at 60-70°C for 24 hours. Complete solution did not occur during the heating period. After cooling, 50 ml of EPC was added and the mixture was filtered, and the solid was collected.

The filtrate was washed with water until the water layer was free of chloride ion. Then the EPC layer was dried over sodium sulfate and then flash evaporated. The resulting oil was vacuum-dried at ambient temperature to give EP-1A (3.56 g.).

The solid obtained during the filtration above was washed with water until the water layer was free of chloride ion and then the solid was vacuum-dried at ambient temperature for 24 hours, to give EP-1B (1.5370 g) as a yellow solid.

On a Fisher-Johns apparatus EP-1A hardened in 30 minutes when a sample was dropped onto the stage preheated to 300°C and in 75 minutes at 250°C. At 200°C the sample did not harden in 4 hours. EP-1B did not melt when dropped onto the stage preheated to 300°C.

On standing for several days EP-1A became more viscous, and eventually changed to a glassy state.

ii. Preparation of Epoxy Resin (EP-2). Reaction of ODA with EPC in the Presence of NaOH (4 moles) for 24 Hours.

According to the procedure given for EP-1 above, ODA (5.0060 g, 0.025 mole), EPC (50 ml) and NaOH (4.00 g, 0.1 mole) were allowed to react for 24 hours. There was obtained EP-2A (2.81 g) as a viscous fluid, and EP-2B (3.8130 g) as a yellow powder.

On a Fisher-Johns apparatus EP-2A hardened in 25 minutes at 300°C and in 60 minutes at 250°C. EP-2B did not melt when dropped onto the stage preheated to 300°C.

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On standing for one week, EP-2A changed to a glassy state.

iii. Preparation of Epoxy Resin (EP-3). Reaction of DAPB-3,4 with EPC in the Presence of NaOH (2 moles) for 24 Hours.

According to the procedure given for EP-1 above, DAPB-3,4 (2.9233 g, 0.01 mole), EPC (50 ml) and NaOH (0.8 g, 0.02 mole) were allowed to react for 24 hours. There was obtained EP-3A (5.171 g) as a viscous fluid and EP-3B (0.6622 g) as a yellow solid.

On a Fisher-Johns apparatus EP-3A hardened in 20 minutes when a sample was dropped onto the stage preheated to 300°C and in 25 minutes at 250°C. At 200°C a sample did not harden in 2 hours. EP-3B did not melt when dropped onto the stage preheated to 300°C.

On standing for one week, EP-3A became a glass.

iv. Preparation of Epoxy Resin (EP-4). Reaction of DAPB-3,4 with EPC in the Presence of NaOH (4 moles) for 24 Hours.

According to the procedure given for EP-1 above, DAPB-3,4 (2.9233 g, 0.01 mole), EPC (50 ml) and NaOH (1.60 g, 0.04 mole) were allowed to react for 24 hours. There was obtained EP-4A (5.32 g) as a viscous fluid and EP-4B (1.644 g) as a yellow solid.

On a Fisher-Johns apparatus EP-4A hardened in 20 minutes when a sample was dropped onto the stage preheated to 300°C and in 30 minutes at 250°C. At 200°C a sample did not harden in 2 hours. EP-4B did not melt when dropped onto the stage preheated to 300°C.

On standing for one week, EP-4A changed to a glassy state.

v. Preparation of Epoxide-Terminated Oligomeric Polyimide (BTEP-4). Reaction of BTAT-6 with EPC in the Presence of NaOH (2 moles) for 24 Hours.

According to the procedure given previously for EP-1, BTAT-6 (2.606 g, 0.001 mole), EPC (50 ml) and NaOH (0.08 g, 0.002 mole) were allowed to react for 24 hours. After cooling, the mixture was filtered. The isolated solid was washed with water until the aqueous layer was free from chloride ion and then the solid was vacuum-dried at ambient temperature to give BTEP-4 (1.0720 g) (as a portion of the solid was accidentally spilled) as a yellow solid. On a Fisher-Johns apparatus BTEP-4 began to melt at 255°C but had not completely melted at 300°C. The drop melt, taken as the lowest temperature at which a sample would completely melt when it was dropped onto the preheated stage of a Fisher-Johns apparatus, was 250°C.

vi. Preparation of Epoxide-Terminated Oligomeric Polyimide (BTEP-5). Reaction of BTAT-6 with EPC in the Presence of NaOH (4 moles) for 24 Hours.

According to the procedure given for EP-1 above, BTAT-6 (2.606 g,

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0.001 mole), EPC (50 ml) and NaOH (0.16 g, 0.004 mole) were allowed to react for 24 hours. There was obtained BTEP-5 (1.8983 g) as a yellow powder. On a Fisher-Johns apparatus BTEP-5 began to melt at 215°C but had not completely melted by 300°C. The drop melt was 250°C.

vii. Preparation of Epoxide-Terminated Oligomeric Polyimide (BTEP-6). Reaction of BTAT-6 with EPC in the Presence of NaOH (2 moles) in Dioxane for 24 Hours.

To a solution of BTAT-6 (2.606 g, 0.001 mole) dissolved in 25 ml of dioxane was added sodium hydroxide (0.0800 g, 0.002 mole) and EPC (0.3700 g, 0.004 mole). The mixture was stirred at 65-70°C for 24 hours during which time the solution changed from orange to yellow, and a precipitate slowly formed. After cooling, the mixture was flash evaporated to give a yellow pasty solid. The pasty solid was washed three times with 25 ml of water and then vacuum-dried at ambient temperature for 24 hours, to give BTEP-6, 2.7052 g, as a yellow powder. BTEP-6 was insoluble in dioxane, DMAC and sulfolane. On a Fisher-Johns apparatus, BTEP-6 melted over the range 200-225°C, thickened above 230°C, and did not harden during 90 minutes at 300°C. The drop melt was 205°C.

viii. Preparation of the Epoxide-Terminated Oligomeric Polyimide (BTEP-7). Reaction of BTAT-6 with EPC in the Presence of NaOH (4 moles) in Dioxane for 24 Hours.

The procedure given above for BTEP-6 was repeated using BTAT-6 (1.578 g, 0.0006 mole), NaOH (0.0935 g, 0.0024 mole), EPC (0.448 g, 0.00485 mole) in 18 ml of dioxane. After following the same isolation procedure, there was obtained BTEP-7, 1.4237 g, as a yellow powder. BTEP-7 was insoluble in DMAC, sulfolane and dioxane. On a Fisher-Johns apparatus BTEP-7 melted over the range 220-260°C, thickened above 280°C, and hardened after 1 hour at 300°C.

ix. Preparation of Epoxide-Terminated Oligomeric Polyimide (BTEP-8). Reaction of BTAT-6 with EPC in the Presence of NaOH (4 moles) in Dioxane for 1 Hour.

The procedure given above for BTEP-6 was repeated using the same amounts of material. However, the heating period was shortened to 1 hour. The same isolation procedure was followed to give BTEP-8 as a yellow powder, 1.5285 g.

On a Fisher-Johns melting point apparatus BTEP-8 melted over the range 195-230°C, thickened and darkened above 260°C, gelled after 5 minutes at 300°C, and did not harden further during 1 hour at 300°C. The drop melt was 225°C.

x. Preparation of Epoxide-Terminated Oligomeric Polyimide (BTEP-9). Reaction of BTAT-6 with EPC in the Presence of NaOH (2 moles) in Dioxane for 24 Hours.

In a 50-ml round-bottom flask was placed a solution of BTAT-6 (1.578 g,

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0.006 mole) and EPC (0.224 g, 0.00122 mole) in 20 ml of dioxane. The solution was heated to 60°C and stirred for 1 hour. Then sodium hydroxide (0.480 g, 0.0012 mole) was added. Heating and stirring at 60°C were continued for 24 hours, during which time the solution became slightly hazy. After cooling the mixture was concentrated on a rotary flash evaporator to give a yellow pasty solid which was washed three times with distilled water and then vacuum-dried at ambient temperature for 24 hours, to give BTEP-9, as a yellow powder, 1.565 g. BTEP-9 was insoluble in DMAC, sulfolane and dioxane. On a Fisher-Johns melting point apparatus BTEP-9 melted over the range 225-250°C.

xi. Preparation of Epoxide-Terminated Oligomeric Polyimide (BTSO-2). Reaction of BTAS-12 [8] with Perbenzoic Acid Generated in Situ.

In a 25-ml round-bottom flask equipped with a capillary air bubbler and a condenser was placed BTAS-12 (1.907 g), 1.0 g of benzaldehyde and 10 ml of methylene chloride. A slow stream of air was bubbled through the solution for 24 hours. Ultraviolet light from a UV lamp (Mineralight; UVS-11) was directed at the flask.

After 24 hours, the methylene chloride was removed by evaporation and the solid was washed five times with 5 ml of anhydrous ether. After vacuum-drying the solid at ambient temperature for 24 hours, there was obtained 1.3390 g of BTSO-2 as a yellow powder. On a Fisher-Johns apparatus, BTSO-2 melted over the range 190-205°C; the drop melt was 195°C.

b. Curing of Epoxy Resins.

i. Curing of Epoxy Resins EP-1A, EP-2A, EP-3A and EP-4A.

Small samples (approximately 0.5 g) of each of the resins EP-1A to EP-4A inclusive were placed into small test tubes. The tubes were flushed with nitrogen, capped with a nitrogen-filled balloon and placed into a metal block preheated to 300°C. After 1 hour the tubes were removed and allowed to cool. All of the resins had melted and darkened. The TGA's in air of each of the cured resins were taken and they are given as Figure 12 for EP-1A-H300, Figure 13 for EP-2A-H300, Figure 14 for EP-3A-H300, and Figure 15 for EP-4A-H300. For comparison, the TGA's in air for ODA and DAPB-3,4 were also determined, and they are given as Figures 16 and 17 respectively.

ii. Post Reactions of Epoxides BTEP-4 to BTEP-9 and BTSO-2.

Small samples of each of the epoxides were placed into small test tubes, the tubes were flushed with nitrogen and capped with a nitrogen-filled balloon. Then the tubes were placed into a preheated metal block. After 1 hour the tubes were removed and allowed to cool. Reactions were also performed in which curing agents were incorporated. The pertinent data, including curing agents and reaction temperatures, are summarized in Table 1. TGA tracings were obtained in air for each of the cured resins, and pertinent data are given in Table 1.

Table 1

Cure Data of Epoxide-Terminated Oligomeric Polyimides

Epoxide-Terminated Oligomer	Cure		TGA in Air			% Wt Loss at 500 °C
	Agent	Temp. °C	Fig. No.	Break °C[a]	Inflection Point °C	
BTEP-4	None	300	18	400	475	12
BTEP-4	1:1 mole m-PDA	250	19	270	450	27
BTEP-5	None	300	20	400	460	16
BTEP-5	5% w/w DMP-30	300	21	350	490	14
BTEP-5	1:2 mole m-PDA	250	22	IND 270	465	27
BTEP-6	1:1 mole m-PDA	225	23	IND 100	545	7
BTEP-7	1:1 mole m-PDA	225	24	150	300 450	31
BTEP-7	1:2 mole m-PDA	250	25	200	250 450	30
BTEP-7	5% w/w Bz$_3$N	225	26	250	470	22
BTEP-8	1:1 mole m-PDA	225	27	260	300 500	27
BTEP-8	1:2 mole m-PDA	250	28	250	300 450	26
BTEP-8	5% w/w Bz$_3$N	225	29	200	430	26
BTEP-9	1:1 mole m-PDA	250	30	300	330 460	21
BTEP-9	5% w/w Bz$_3$N	250	31	300	320 450	26
BTSO-2	None	225	32	350	580	2
BTSO-2	5% w/w Bz$_3$N	225	33	350	565	4
BTSO-2	1:1 mole m-PDA	225	34	400	595	3

a: IND = Indefinite but located in region of temperature shown.

2. Chain Extension of Reactive End-Capped Oligomeric Polyimides.

a. Melt Reaction of BTPN-1 with Copper Metal.

An intimate mixture of BTPN-1 (0.7274 g, 0.0003 mole) and copper powder (0.0127 g, 0.0002 mole) was prepared in a wig-L-jig mixer mill. The mixture was transferred to a pyrex reaction vessel which was flushed with nitrogen and capped with a nitrogen-filled balloon. Then the filled tube was placed into a metal block preheated to 300°C and maintained at 300°C for 1 hour. The sample melted completely and darkened. After cooling there was obtained a dark-green solid which was insoluble in m-cresol, and which did not melt but softened slightly when dropped onto the stage of the Fisher-Johns apparatus preheated to 300°C. The TGA in air is given as Figure 35 and the TGA in nitrogen is given as Figure 36.

b. Reaction of BTPN-1 with Cuprous Chloride in m-Cresol.

Into a 50-ml round-bottom flask was placed BTPN-1 (0.5156 g, 0.0002 mole), Cu_2Cl_2 (0.0213 g, 0.0001 mole, corrected for 93% assay) and 10 ml of m-cresol. The mixture was heated at reflux for 18 hours, during which time the reaction mixture became green and hazy. After cooling, the mixture was transferred to a pyrex reaction tube which was placed into a metal block. Heating was begun and the block temperature was raised to 300°C over 4 hours, during which time m-cresol was distilled off. Then the temperature was maintained at 300°C for 1 hour. After cooling, there was obtained a dark-green solid which was insoluble in m-cresol and which did not melt but softened slightly when a sample was dropped onto the stage of the Fisher-Johns apparatus preheated to 300°C. The TGA in air is given as Figure 37, and the TGA in nitrogen is given as Figure 38.

c. Curing of BTAS-16.

A 0.100 g sample of BTAS-16 was heated at 250°C in a nitrogen-filled test tube for 15 minutes. The sample melted and darkened. After cooling, the sample was placed on the stage of a Fisher-Johns apparatus and progressively heated. The sample did not melt at temperatures up to 300°C, but it softened to an elastic mass at 270°C and remained elastic after heating for 10 minutes at 300°C; it was insoluble in hot m-cresol. The TGA in air is given as Figure 39 and the TGA in nitrogen is given as Figure 40.

3. Polyimides.

a. Preparation of PI-25. Reaction of BTCA and BAPS-4,3 (1:1).

According to the m-cresol:azeotropic technique [8], BTCA (0.8055 g, 0.0025 mole) and BAPS-4,3 (1.0812 g, 0.0024 mole; Sample B of II.A.13) in 25 ml of m-cresol and 15 ml of benzene. After refluxing for 3 hours, approximately 0.1 ml of water had been collected (theory = 0.09 ml) and the reaction mixture was a clear red solution. The solution was made up to 50 ml with m-cresol and divided into two 25 ml fractions.

One fraction was added to 100 ml of stirred cyclohexane. The cyclohexane was decanted and the residue was digested again in 100 ml of warm cyclohexane and twice in 100 ml of methanol. The solid residue was filtered

off, washed with methanol and vacuum-dried at 70°C for 24 hours, to yield PI-25A, 0.6980 g (77%) as a pale-yellow powder. On a Fisher-Johns melting point apparatus, PI-25A melted over the range 220-240°C, and thickened and darkened slightly but did not harden in 1 hour at 300°C. PI-25A was soluble in m-cresol, sulfolane, DMAC and dioxane; insoluble in chloroform and methylene chloride; swelled in hot methyl ethyl ketone; $[\eta]_{inh}$ (0.5% m-cresol) = 0.187 dl/g. The TGA tracings in air and in nitrogen are given as Figures 41 and 42 respectively.

Analysis: Calc'd for $C_{41}H_{22}N_2O_9S$ (PI-25A)

C, 68.52; H, 3.09; N, 3.89; O, 20.03; S, 4.46.

Found: C, 67.89; H, 3.23; N, 4.04; O, -----; S, -----.

b. Bodying of PI-25.

The remaining portion of the solution of PI-25 above was heated to distill off approximately one-half of the solvent. Then the concentrated solution was heated at reflux for 24 hours, during which time the solution increased noticeably in viscosity. After cooling there was obtained a dark, thick solution which was poured into 100 ml of stirred 1:1 methanol-cyclohexane. After stirring for 15 minutes, the solid was filtered off and digested three times in 100 ml of 1:1 methanol-cyclohexane and then vacuum-dried at 70°C for 24 hours, to yield PI-25B, 0.780 g (86%), $[\eta]_{inh}$ (0.5% m-cresol) = 0.234 dl/g, as a tan solid which was soluble in m-cresol, DMAC, sulfolane and dioxane, and was insoluble in methyl ethyl ketone. On a Fisher-Johns apparatus, PI-25B melted over the range 225-250°C and did not harden in 1 hour at 300°C. The TGA in air is given as Figure 43 and the TGA in nitrogen is given as Figure 44. The infrared spectrum of PI-25B is given in Figure 45.

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SECTION III

DISCUSSION

A. Intermediates.

Additional quantities of 1,3-di(4-aminophenoxy)benzene (DAPB-3,4) were required for conversion to epoxy derivatives, EP-3 and EP-4. 1,3-Di(3-aminophenoxy)benzene (DAPB-3,3) was required for the preparation of an amine-terminated oligomeric polyimide, BTAT-6, to be converted to epoxy derivatives, BTEP-4, -5, -6, -7, -8 and -9, and for the synthesis of a styrene-terminated oligomeric polyimide, BTAS-12, for conversion to the epoxide derivative, BTSO-2. The previously reported procedure [3] was used to prepare DAPB-3,4 and its dinitro precursor DNPB-3,4 [2]. These procedures [2,3] were reproducible with regard to quality and yield of products.

The contribution of oxygen linkages in DAPB-3,4 and of the sulfone linkage in 3,3'-sulfonyldianiline (SDA-3,3) to the tractability of the aromatic polyimides derived by condensation with di-anhydrides, prompted the syntheses of diamines of the formula

$$H_2NC_6H_4OC_6H_4SO_2C_6H_4OC_6H_4NH_2 \quad (BAPS)$$
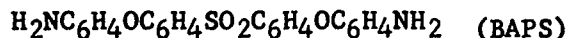
which were expected to improve the tractability of the oligomers.

A previous attempt [10] to prepare the precursor nitro compound (a BNPS-type intermediate) by the reaction of 4,4'-sulfonyldiphenol with 1,3-bromonitrobenzene was not successful, even though the analogous reaction for the preparation of DNPB-3,4, the dinitro precursor to DAPB-3,4, was very successful [3].

Five additional attempts were made to prepare BNPS-type dinitro precursor compounds. In two attempts, the sodium salt of p-nitrophenol was used as a reactant with 4-chlorophenylsulfone. When the reaction was attempted either in refluxing methyl ethyl ketone or in refluxing diglyme, only unreacted 4-chlorophenyl sulfone was isolated.

Two additional reactions between the sodium salt of 4,4'-sulfonyldiphenol and 1,3-bromonitrobenzene in refluxing diglyme were attempted. In the first reaction, no catalyst was used, whereas, in the second reaction, cuprous chloride was incorporated as a catalyst. Cuprous chloride has been used as a catalyst in the synthesis of DNPB-type compounds [11]. However, in both these cases, only unreacted starting materials were recovered.

A fifth attempt was made to prepare a dinitro precursor, specifically BNPS-4,4, using an adaptation of a recently reported procedure [12] which had been used to prepare polymers from 4-chlorophenyl sulfone and bis-phenols. The reaction was unsuccessful and yielded only an unidentified tarry product.

The failure of the reaction between 4-chlorophenyl sulfone and sodium-p-nitrophenoxide may be due to the presence of the strongly electron-attracting

nitro group. Accordingly, two intermediates, 3- and 4-hydroxyacetanilide, were prepared for evaluation in reactions, as the sodium salts, with 4-chlorophenyl sulfone. If successful, the reaction would afford a diacetamide derivative, for example, bis[4-(3-acetamidophenoxyl)phenyl] sulfone (BACS-4,3), which on hydrolysis of the acetamido group, would yield the desired corresponding diamine bis[4-(3-aminophenoxy)phenyl] sulfone (BAPS-4,3).

No difficulties were encountered in preparing 3- or 4-hydroxyacetanilide using published procedures [4].

The attempted preparation of BACS-4,4 from 4-chlorophenylsulfone and the sodium salt of 4-hydroxyacetanilide at 135-140°C for 6 hours in the presence of pyridine and diglyme afforded only starting materials. The same reaction, attempted in DMF as a solvent, yielded only starting materials.

The next attempt was the synthesis of bis[4-(3-acetamidophenoxy)phenyl] sulfone via an adaptation of the reaction used to prepare the DNPB-type intermediates [11] and was run in pyridine with cuprous chloride catalysis. A 98% recovery of unreacted 4-chlorophenyl sulfone was obtained.

In the next reaction, 4-chlorophenyl sulfone was allowed to react with the sodium salt of 3-hydroxyacetanilide in DMF with cuprous chloride as the catalyst. A material was obtained in relatively low yield (30.3%) whose infrared spectrum contains bands for the amide function, as well as bands for the sulfone group. A sample of this material was hydrolyzed with concentrated hydrochloric acid to afford approximately a 100% yield of the hydrochloride from which the diamine was generated in a 93% yield, as a red, glassy material. Since a thin layer chromatogram showed several bands, the material was chromatographed on a silica gel column to yield a number of fractions. On the basis of infrared spectra and thin layer chromatograms, fractions I and II were combined into Sample A; fraction III was labelled Sample B. The weight of Sample A was 3.798 g, the weight of Sample B was 2.234 g, and residues of 0.0053 g from later fractions amounted to a total of 6.0373 g from an original feed to the column of 6.350 g. Sample A was a white powder and Sample B was a red glass. The analysis of Sample B indicated that the desired compound had been attained. The wide melting point range of 65-75°C for Sample B appears to be the result of a mixture of isomers due to benzyne-type intermediates. In the presence of strongly basic conditions and high temperatures, the 4-chlorophenyl sulfone may undergo reaction via an elimination-addition mechanism (benzyne-type intermediate) to yield 3- and 4-substituted phenyl sulfones, as well as via a substitution mechanism which would yield the 4-substituted phenyl sulfone. The analysis of Sample A suggested that it was contaminated with hydrochloride(s) of the diamine, whose presence was confirmed by tests for halogen. The presence of halogen also indicated that a modification of the treatment of the dihydrochloride was required to assure complete liberation of the diamine. This and other modifications were made in the subsequent synthesis to prepare additional quanties of BAPS-4,3.

The modifications consisted of an increased amount of cuprous chloride catalyst in the initial condensation and minor changes in the hydrolysis and neutralization steps. The overall effect was to increase the yield of the precursor, BACS-4,3 from 30.3% to 91.5% and a resulting increase in the yield of isolated BAPS-4,3 from the BACS-4,3 of 8.4% to 14.0%. The second

synthesis gave an apparently more crystalline material, almost white in color with an improved melting point. These improvements may be due to the increased catalyst ratio which could influence the relative amounts of products formed via substitution and benzyne-type reaction pathways as discussed above.

The above results indicate that the yields can be increased to higher values by additional studies as was accomplished in the synthesis of DAPB-3,3 [11]. These studies, as well as the synthesis of the isomeric bis[3-(3-aminophenoxy)phenyl] sulfone (BAPS-3,3), which would be analogous to DAPB-3,3, could not be undertaken at this time within the limitations of this program.

APN (4-aminophthalonitrile) was desired as a reactant for end-capping oligomeric polyimides, which, in turn, were to be converted to polymers by the formation of phthalocyanine bridges.

APN has been reported in the literature [7] and the method followed in this research is a modification of the published work. The reaction sequence involved the conversion of 4-nitrophthalimide (NPI) to 4-nitrophthalamide (NPA) by reaction with aqueous ammonia; dehydration of NPA to 4-nitrophthalonitrile (NPN) via thionyl chloride in DMF, and finally, reduction of the NPN to APN.

The preparation of NPA presented no problems and the NPA was obtained in high yields. In the literature report cited [7] NPA was converted to NPN by refluxing in acetic anhydride for 20 hours with a reported yield of 51%.

In the conversion of NPA to NPN three modifications of a method reported [13] to be successful for the conversion of phthalamide to phthalonitrile have been carried out. All involve the use of thionyl chloride in DMF as the dehydration agent. In the most successful modification, the yield of NPN was 73% and the product was of sufficient quality to use without additional purification.

In the report cited [14] NPN was reduced to APN with sodium hydrosulfite, although no particulars of the reaction were given, and the product melted over a 10°C range. One attempt to perform such a reduction was conducted and a material was obtained in 35.6% yield whose infrared spectrum conformed to that expected for APN. In addition, another material was obtained in approximately the same amount, whose infrared spectrum indicates that some hydrolysis of the nitrile groups occurred.

The first attempt at the catalytic reduction of 4-nitrophthalonitrile yielded a product which displayed infrared absorption bands for both amino and nitro groups, indicating incomplete reduction. Apparently, the catalyst becomes inactivated during the reduction. However, when the reduction was performed by adding the catalyst in two stages, the reduction was successful and yielded the desired compound in good yields and of high purity.

B. Oligomers.

The m-cresol:azeotropic technique [8] was used to prepare the required oligomers. This technique has high reproducibility and no difficulties were encountered in the syntheses of oligomers BTAT-6, BTAS-12, BTAS-16 and BTPN-1.

C. Polymers.

1. Epoxy Systems.

A study was undertaken to determine the feasibility of epoxidizing the amino groups of amine-terminated oligomeric polyimides directly with epichlorohydrin. Such amine-terminated oligomers can be prepared readily solely from the dianhydride and the diamine as reactants [8] and would eliminate the use of aminophenols which are required for the phenol-terminated oligomers [8], which also have been converted to epoxide derivatives [16]. The softening points of the epoxides derived from phenol-terminated oligomeric polyimides were noticeably higher than their phenolic precursors. It was hoped that the epoxidizing amine-terminated oligomeric polyimides would have lower softening points than their phenolic counterparts. The epoxidation of the amine moieties can be represented as occurring as follows:

$$ArNH_2 + ClCH_2CHCH_2 \xrightarrow{\text{base}} ArNHCH_2CHCH_2 \xrightarrow[\text{base}]{ClCH_2CHCH_2} ArN(CH_2CHCH_2)_2.$$

The reactions of two diamines, ODA and DAPB-3,4 with epichlorohydrin in the presence of sodium hydroxide, as the hydrohalide acceptor, were performed as prototype reactions. The reactions were performed in two manners. According to the first procedure, one molar equivalent of the diamine was allowed to react in an excess of EPC as solvent in the presence of two molar equivalents of sodium hydroxide. In the second procedure, the molar ratio of diamine to sodium hydroxide was changed to 1:4. Epoxy resins EP-1 and EP-3 were obtained according to the first procedure using ODA and DAPB-3,4 respectively, while resins EP-2 and EP-4 were obtained according to the second procedure, using ODA and DAPB-3,4 respectively.

Each of the four reactions gave two fractions, a viscous oily (fraction A) and a powdery insoluble solid (fraction B). All of the oily fractions gradually became more viscous and then changed to a glassy state after standing for 1 week at room temperature. The solid fractions did not melt when dropped onto the stage preheated to 300°C and appear to be cured epoxides. The amounts of solid, obtained from reactions performed in the presence of 4 molar equivalents of sodium hydroxide, were a greater portion of the total weight of products than those obtained using 2 molar equivalents of sodium hydroxide. Also, the amount of insoluble residue obtained when DAPB-3,4 was used as the diamine, was considerably less than when ODA was used.

Then, the study of the reactions of diamines with epichlorohydrin to form epoxides was continued with the amine-terminated oligomeric polyimide. BTAT-6 (based on BTCA and DAPB-3,3) was allowed to react with an excess of epichlorohydrin in the presence of 2 molar and 4 molar equivalents of sodium hydroxide. The reactions were performed in two basic manners. In the first procedure, the amine-terminated oligomeric polyimide and sodium hydroxide were heated at 60-70°C for 24 hours in a large excess of epichlorohydrin. The epichlorohydrin was used both as reactant and as solvent. According to the second procedure, the amine-terminated oligomeric polyimide was dissolved in dioxane and then the epichlorohydrin and sodium hydroxide were added and the resulting mixture was heated at 65-70°C for 24 hours. Thus,

21

BTEP-4 (m.p. approximately 225°C) and BTEP-5 (m.p. approximately 215°C) were prepared by the first procedure utilizing 2 molar and 4 molar equivalents of sodium hydroxide respectively.

BTEP-6 (m.p. 220-225°C) and BTEP-7 (m.p. 220-260°C) were prepared by the second procedure utilizing 2 molar and 4 molar equivalents of sodium hydroxide respectively. The products obtained by the first procedure were higher melting than the corresponding products obtained by the second procedure. All four of the epoxide-terminated oligomeric polyimides melted at higher temperatures than the original amine-terminated oligomeric polyimide, BTAT-6, which melted over the range 180-200°C [8].

In order to determine whether the desired products were chain-extending during the long heating period, the preparation of BTEP-8 was undertaken with a heating period of 1 hour, according to the second procedure, using 4 molar equivalents of sodium hydroxide. BTEP-8 (m.p. 195-230°C) was lower melting than BTEP-7 (m.p. 220-260°C), which was heated for 24 hours, but was still higher melting than BTAT-6 from which it was prepared.

The epoxide-terminated oligomeric polyimide, BTEP-9, was prepared by a modification of the method used to prepare BTEP-8. The modification consisted of allowing the BTAT oligomer to react for a period of time with the EPC before the addition of the sodium hydroxide. During the preparation of BTEP-6, in which the sodium hydroxide was present initially, a precipitate formed in the course of the heating period. In the preparation of BTEP-9, however, the reaction solution became only slightly hazy. However, BTEP-9 (m.p. 225-250°C) was somewhat higher melting then BTEP-6 (m.p. 220-225°C).

Another epoxide-terminated oligomeric polyimide, BTSO-2, was prepared by the oxidation of a styrene-terminated oligomeric polyimide, BTAS-12, by perbenzoic acid. The perbenzoic acid was formed in situ by the reaction of benzaldehyde and air under the influence of ultraviolet light. BTSO-2 was obtained as a yellow powder whose melting point was slightly higher than the original BTAS-12 [9].

Attempts to determine the epoxy content were discontinued; a previous attempt with a related epoxide-terminated oligomeric polyimide gave erroneous values, probably due to some hydrolysis of the imide linkages [15].

Each of the epoxides was then cured. The monomeric bis-epoxides were cured thermally at 300°C. The mechanism of curing was through the secondary amine functions in EP-1A and EP-3A, and through the tertiary amine functions in EP-2A and EP-4A. The TGA values in air (Figures 12-15) of the cured resins were performed and showed that the cured resins were considerably more thermally stable than their diamine precursors (Figures 16-17). In addition, the TGA values showed that when the molar ratio of diamine to sodium hydroxide was 1:4 the resins, after curing, were slightly more thermally stable than those obtained from reactions using a 1:2 molar ratio of diamine to sodium hydroxide. The TGA inflection points of ODA and DAPB-3,4 in air were about 200°C; the highest corresponding value for the monomeric bis-epoxide was 360°C for EP-3A.

The oligomeric polyimides were cured thermally without the addition of other agents, as well as by the addition of a coreactive curing agent, specifically, m-phenylenediamine (m-PDA) and also by the use of catalytic curing agents such as 2,4,6-tri-(dimethylaminomethyl)phenol (DMP-30) and tribenzylamine (Bz$_3$N).

The curing temperature used was selected at about 20°C above the melting or softening point of the oligomer. Thermogravimetric analyses in air at the rate of 10°C per minute were performed on the cured epoxy products.

In general, for the BTEP series, the oligomeric epoxides cured in the absence of curing agents exhibited better thermal properties than those compositions to which curing agents, such as m-PDA, Bz$_3$N and DMP-30 had been added. This can be attributed to the structures of the N-epoxide derivatives, -NHCH$_2$CH$_2$ and -N(CH$_2$CH$_2$CH$_2$)$_2$, which have basic character and thus are auto-catalytic for the curing of the epoxide. In those cases in which 2 moles of m-PDA were used as the curing agents for the tetra-epoxy-substituted oligomer, breaks occurred in the lower temperature regions of the TGA tracings, apparently due to loss of unreacted m-PDA. Similar losses were observed in some cases when Bz$_3$N and DMP-30 were used as curing agents. The TGA data, as shown for example, in Figures 18, 20 and 21 with inflection points in air in the 450-475°C region, warrant continuation of studies on these epoxy derivatives of amine end-capped oligomeric polyimides, particularly with reference to the parameters in synthesis and curing.

The TGA thermal stability in air of the BTSO-type of epoxy-terminated oligomeric polyimide, prepared by epoxidizing a styrene-terminated oligomeric polyimide was higher than any of the BTEP series of epoxidized oligomeric polyimides. The only one of this series prepared was BTSO-2, for which the thermal stability data are given in Figures 32, 33 and 34. BTSO-2 cures well thermally at 225°C as well as in the presence of Bz$_3$N and m-PDA, showing inflection points in the 565-595°C region in air. Although the BTSO oligomers are more difficult to synthesize than the BTEP series, they warrant further consideration and study.

The phthalonitrile end-capped oligomeric polyimide (BTPN-1), was subjected to a melt reaction at 200°C with metallic copper on the basis of 3 moles of BTPN-1 to 2 moles of copper metal. A green complex typical of copper phthalocyanine was obtained, which was insoluble in hot m-cresol, indicating that crosslinking had occurred. The TGA in air of the cross-linked polymer is given in Figure 35, and shows a break in the tracing at 375°C and an inflection point in the 480°C region, which values are almost identical to those shown in Figure 36 in a nitrogen atmosphere. The values in Figure 35 and Figure 36 represent a substantial improvement over the values shown for BTPN-1 in Figure 9 before conversion to the copper complex.

A green copper complex of BTPN-1 was also obtained when it was reacted with cuprous chloride in a m-cresol solution. The complex was isolated by removal of the m-cresol by distillation, leaving an insoluble, infusible product, which retained some quantity of cresol as shown by its TGA tracings in Figure 37 for air and Figure 38 for nitrogen. In these cases, the inflection points are lower than the values obtained on the product of the melt reaction.

A sample of BTAS-16, the styrene end-capped oligomeric polyimide based on the new diamine, BAPS-4,3, was cured by heating under nitrogen at 250°C for 15 minutes; it became insoluble in hot m-cresol. At 250°C, the product was hard, but at 270°C and up to 300°C, the cured product exhibited some elasticity. This behavior probably reflects the character of the
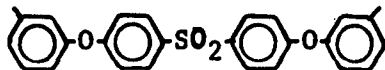
structure contributed by the diamine to the polymer. The TGA in air, given in Figure 39, shows an inflection point in the 475°C region.

In the uncured molten stage, BTAS-16 shows more flow, when pressure is applied to it on the stages of a Fisher-Johns apparatus than a similar polymer made with DAPB-3,3.

The limitations of this research program did not permit the synthesis of the BAPS-3,3 isomer,
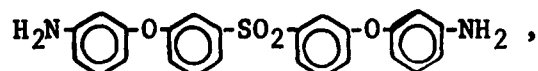
which, it is believed, would contribute more tractability to the polymer than did the BAPS-4,3 diamine; this effect would be expected to parallel the increased tractability that DAPB-3,3 contributed over DAPB-4,3 to oligomeric polyimides.

The polyimide PI-25, based on the new diamine BAPS-4,3, displayed about the same solubility as PI-17 [17] and PI-20 [18] which were based on DAPB-3,3. However, in the molten condition on the metal stage of a Fisher-Johns apparatus, PI-25 appeared to flow more readily when pressure was applied than did PI-17 and PI-20. Also, PI-25 as prepared had a low inherent viscosity as did PI-20, but similarly, it was demonstrated that PI-25 could be bodied to higher viscosities by elimination of m-cresol, and continued heating. The bodying of PI-25 from an initial $[\eta]_{inh}$ of 0.187 dl/g to 0.234 dl/g was easily accomplished, after which the bodying experiment was terminated. If desired, the bodying could be continued to higher inherent viscosity values.

The TGA thermogram of PI-25A in air (Figure 41) closely resembles the tracings of PI-20 except that it shows a higher retention of 4% m-cresol up to about 200°C. Its TGA inflection point in air is in the 480°C region.
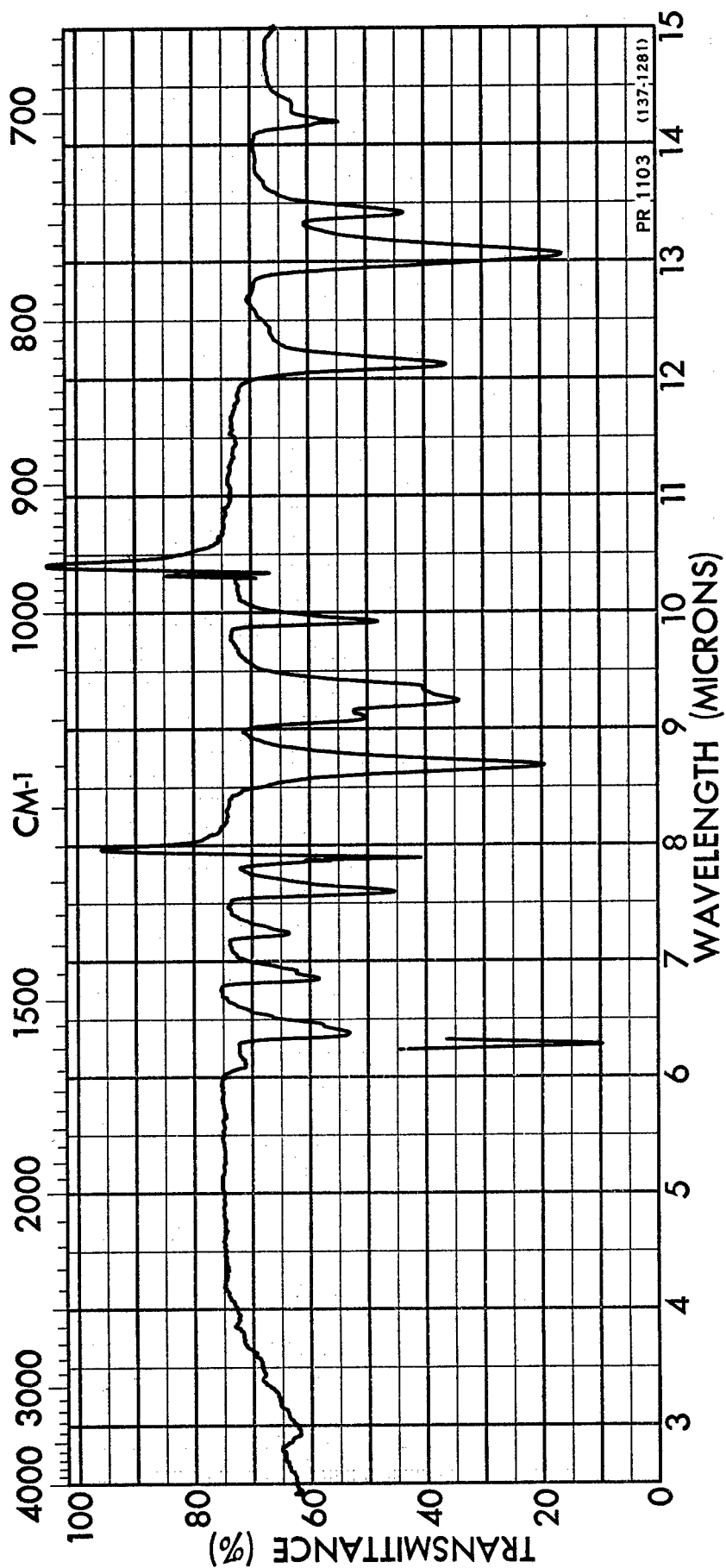
Figure 1. Infrared Spectrum of 4-Chlorophenyl Sulfone (KBr disc).

PR 1103   (137-1281)

25
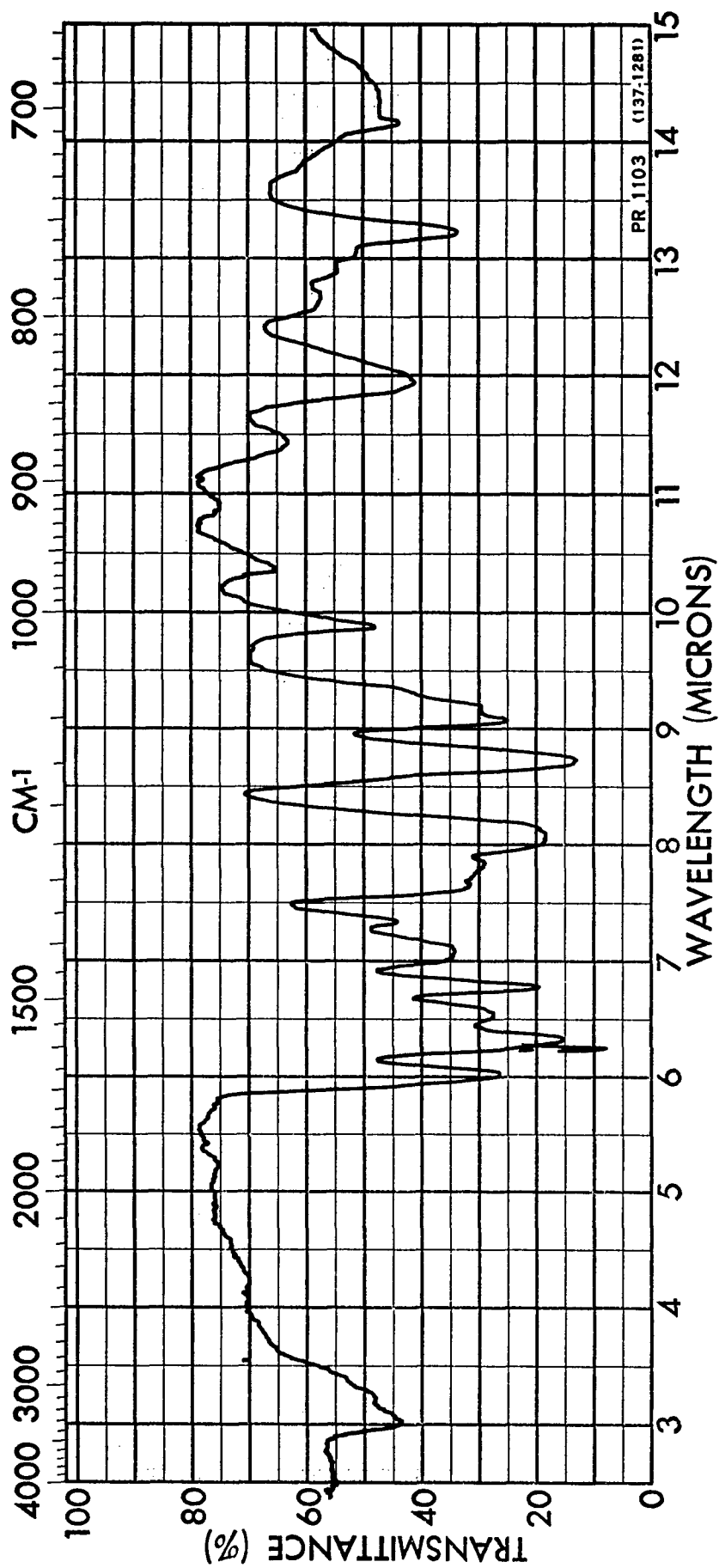
Figure 2.   Infrared Spectrum of BACS-4,3 (KBr disc).

PR 1103   (137-1281)

26
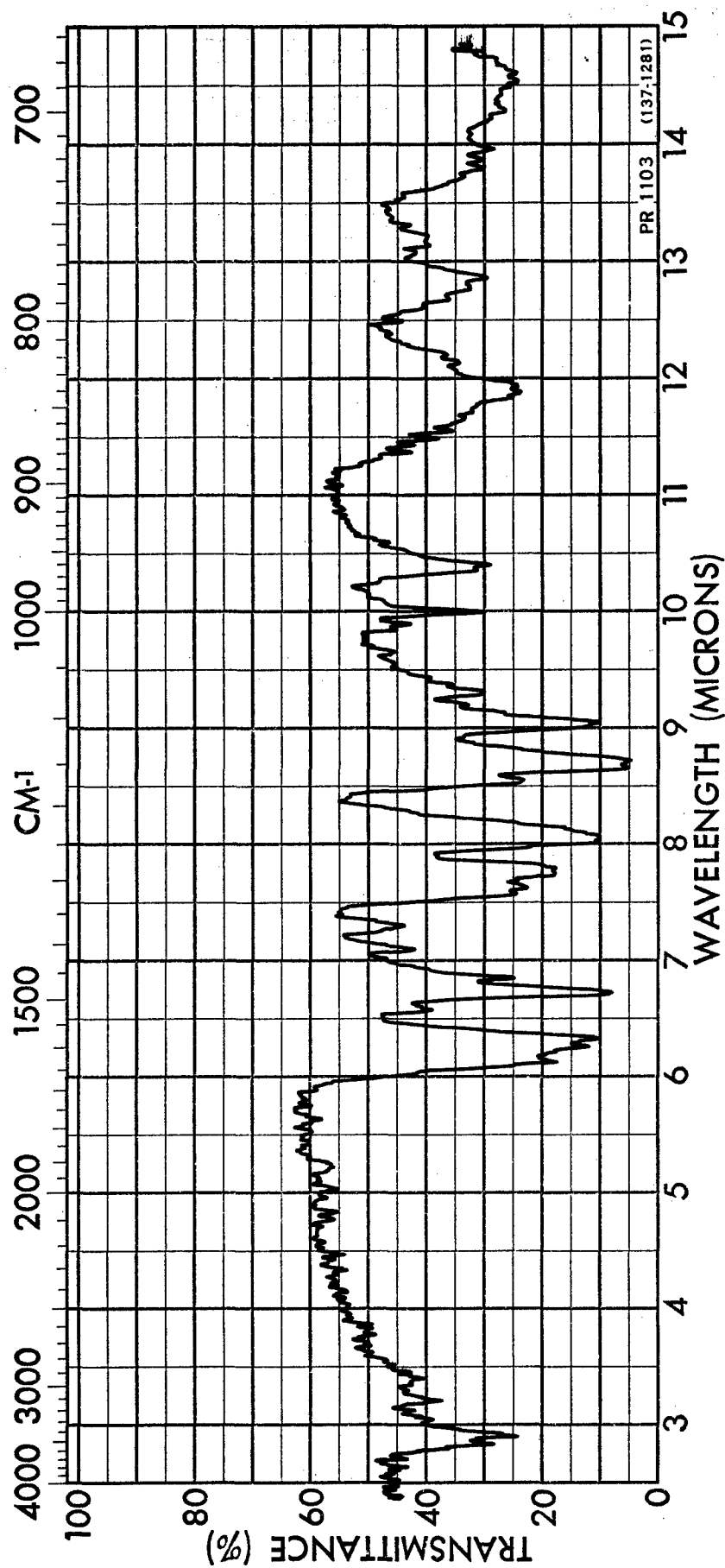
Figure 3. Infrared Spectrum of BAPS-4,3 (KBr disc).

PR 1103   (137-1281)

27
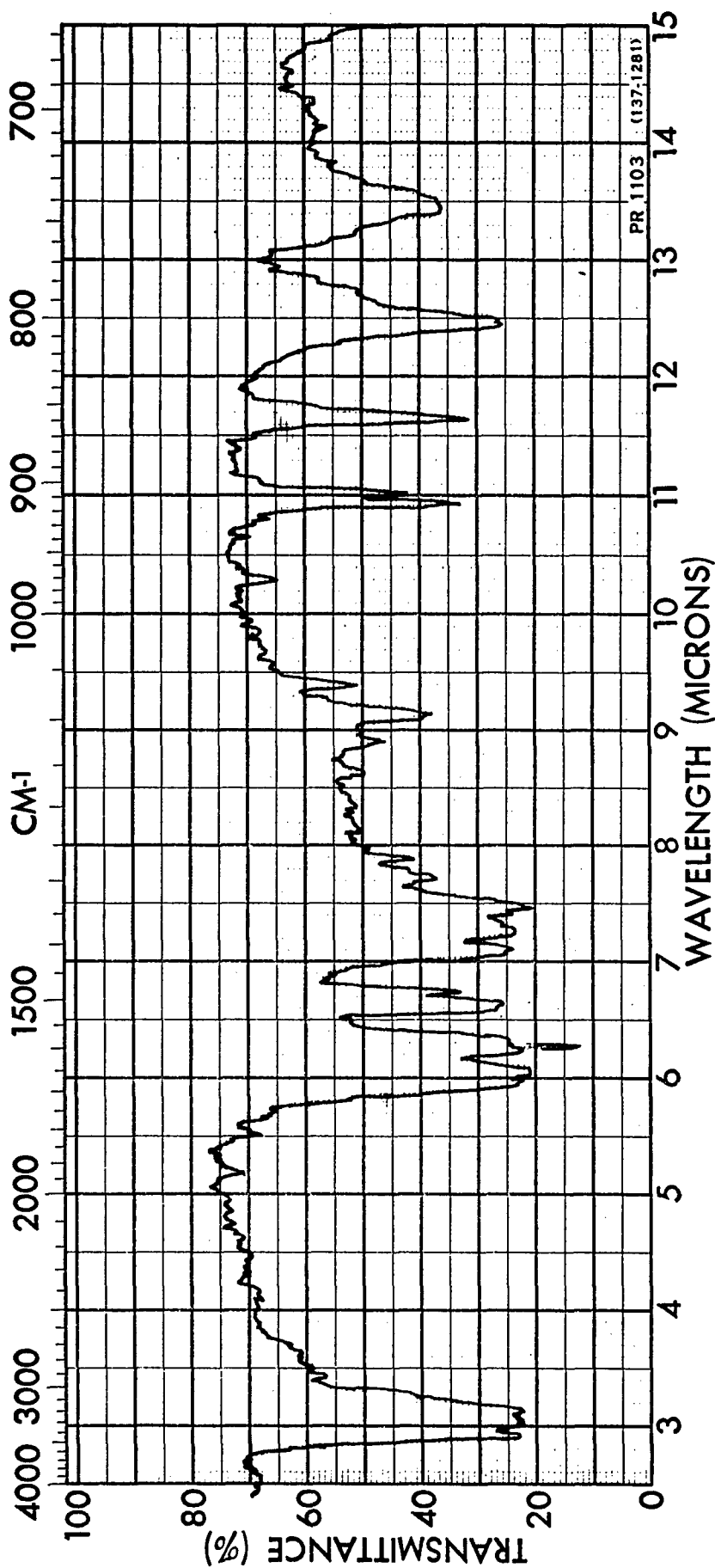
Figure 4.   Infrared Spectrum of 4-Nitrophthalamide (KBr disc).
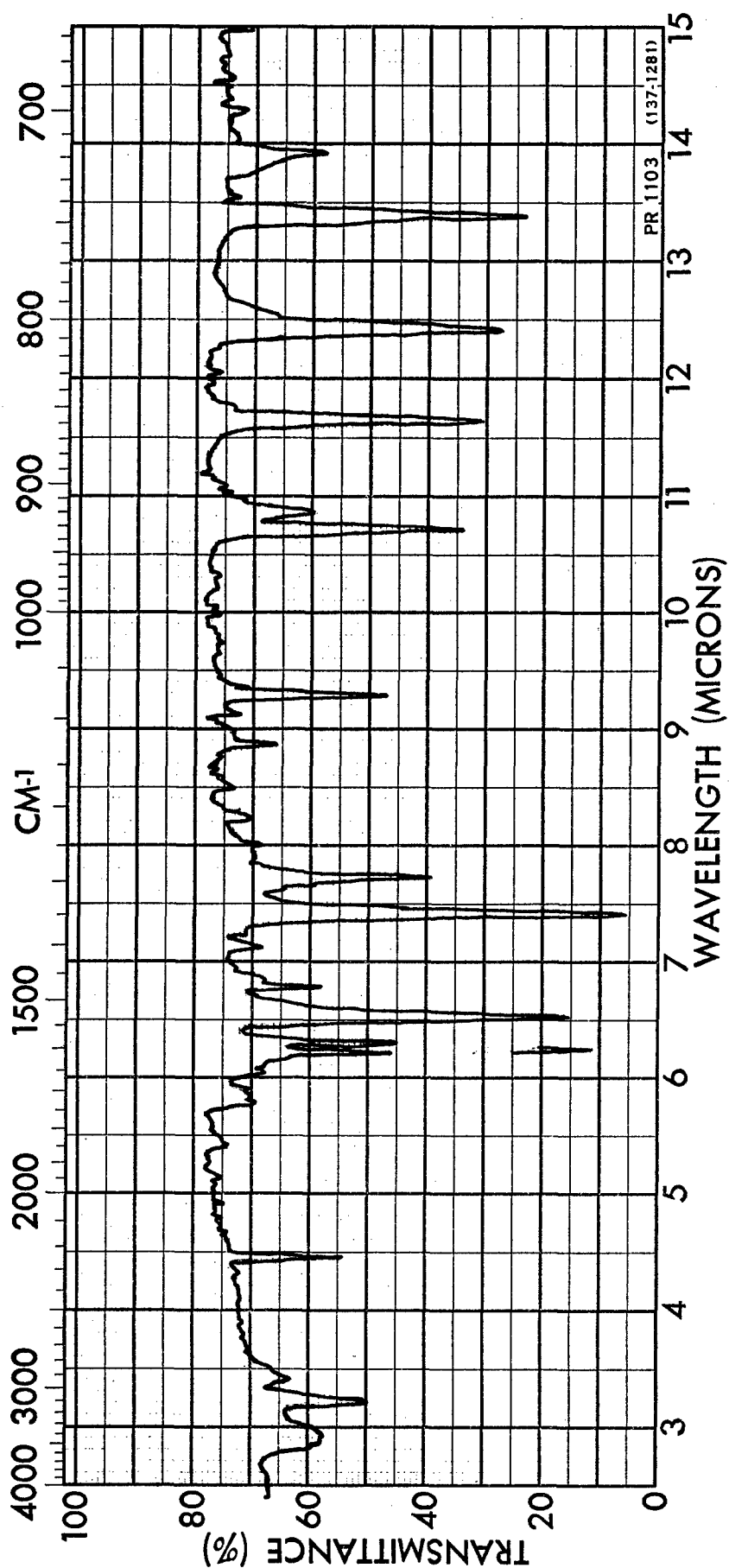
Figure 5.   Infrared Spectrum of 4-Nitrophthalonitrile (KBr disc).

29
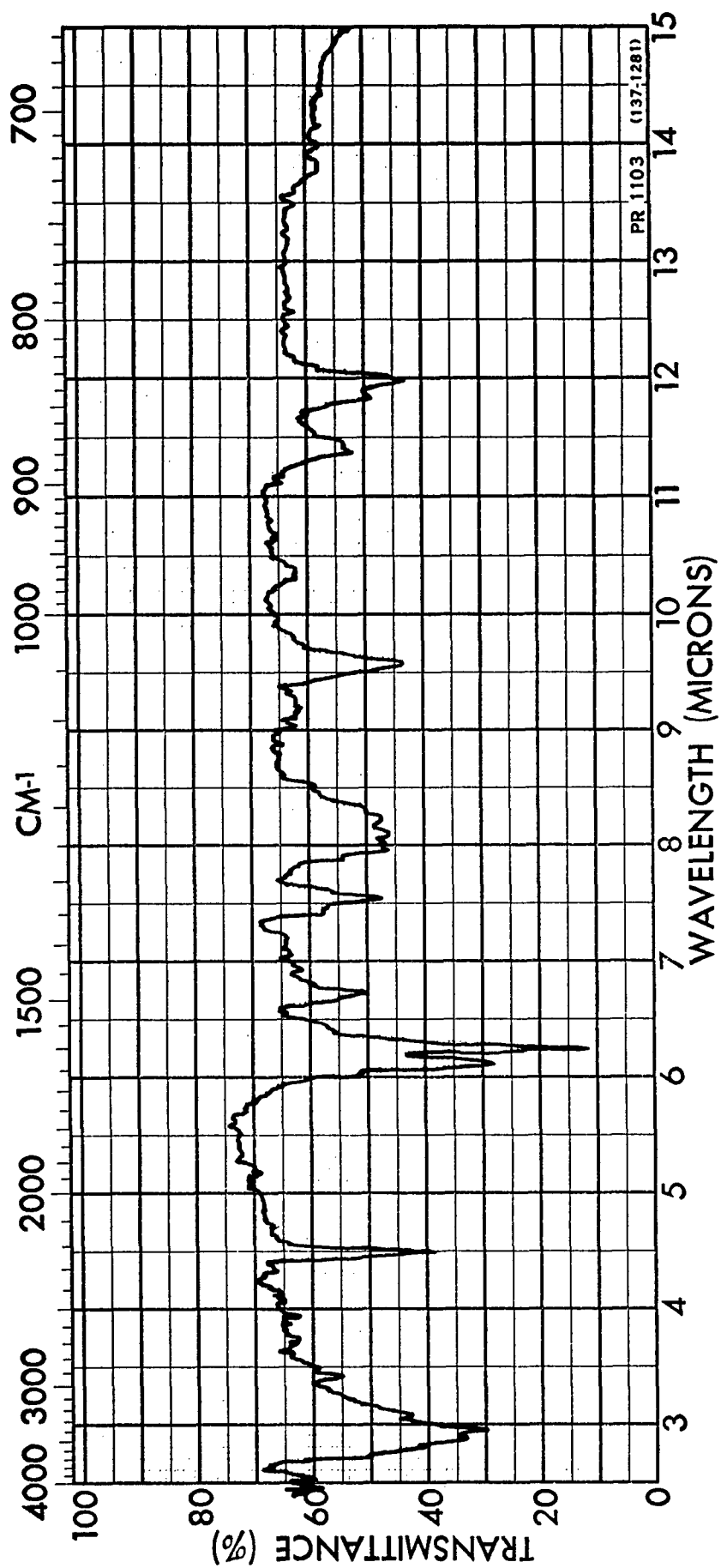
Figure 6. Infrared Spectrum of 4-Aminophthalonitrile (KBr disc).

PR 1103 (137-1281)

30
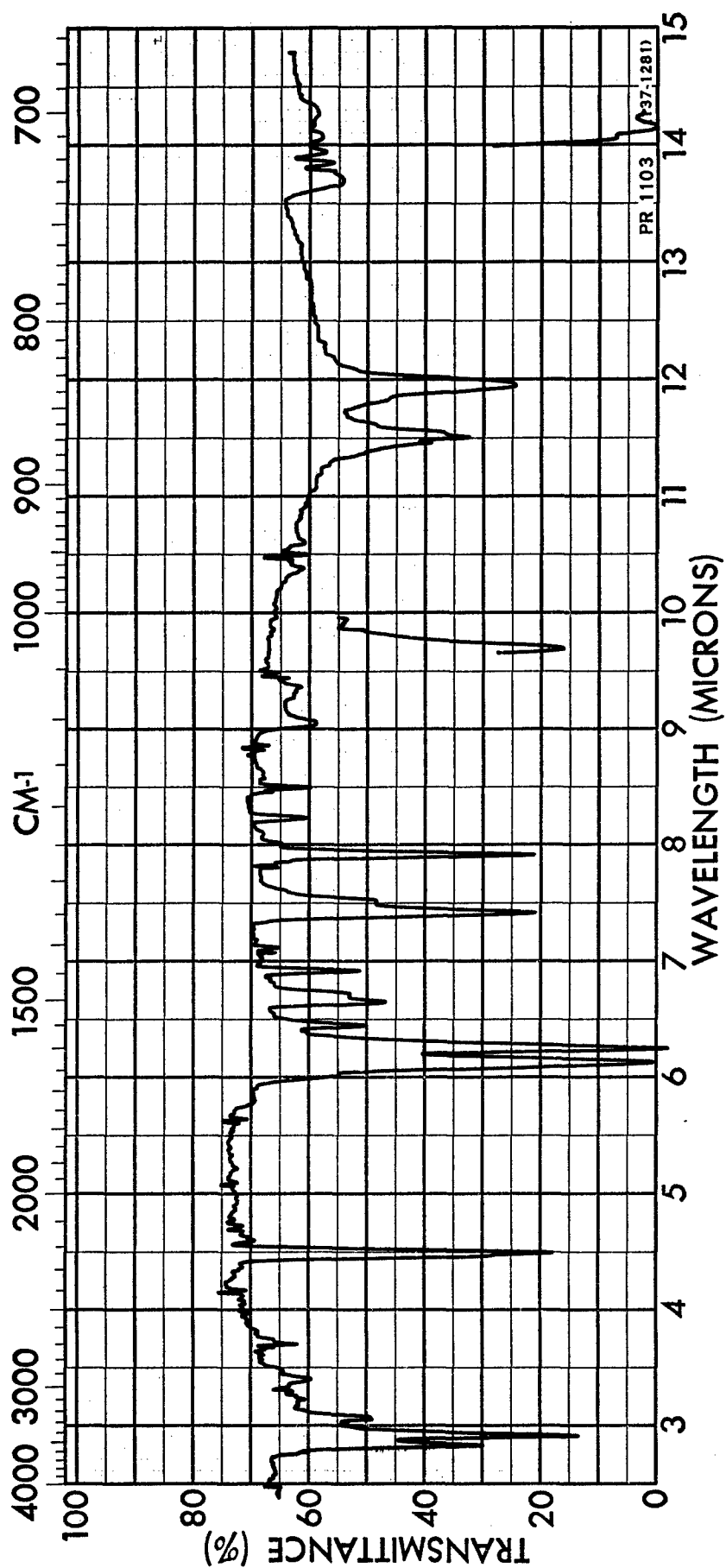
Figure 7. Infrared Spectrum of 4-Aminophthalonitrile (KBr disc).

31
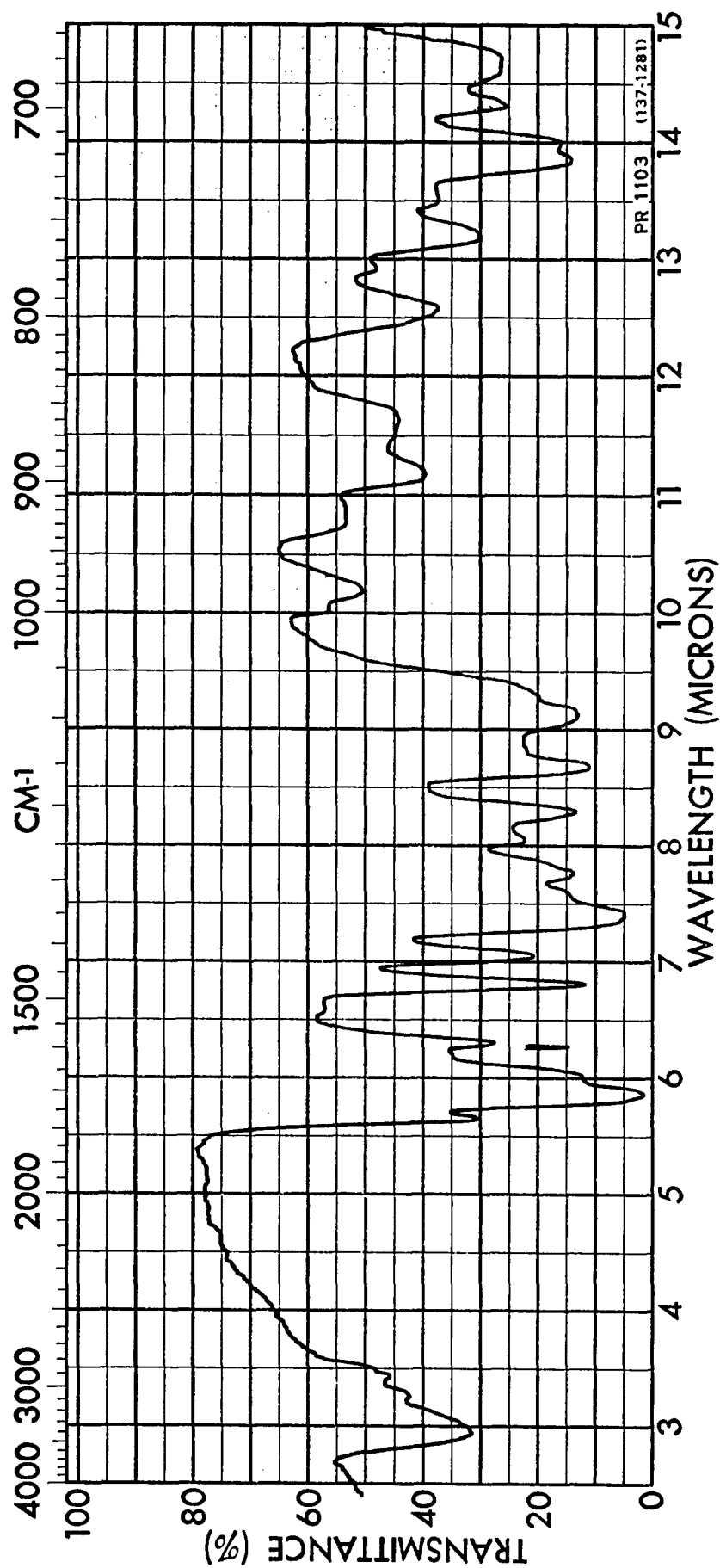
Figure 8. Infrared Spectrum of BTPN-1 (KBr disc).
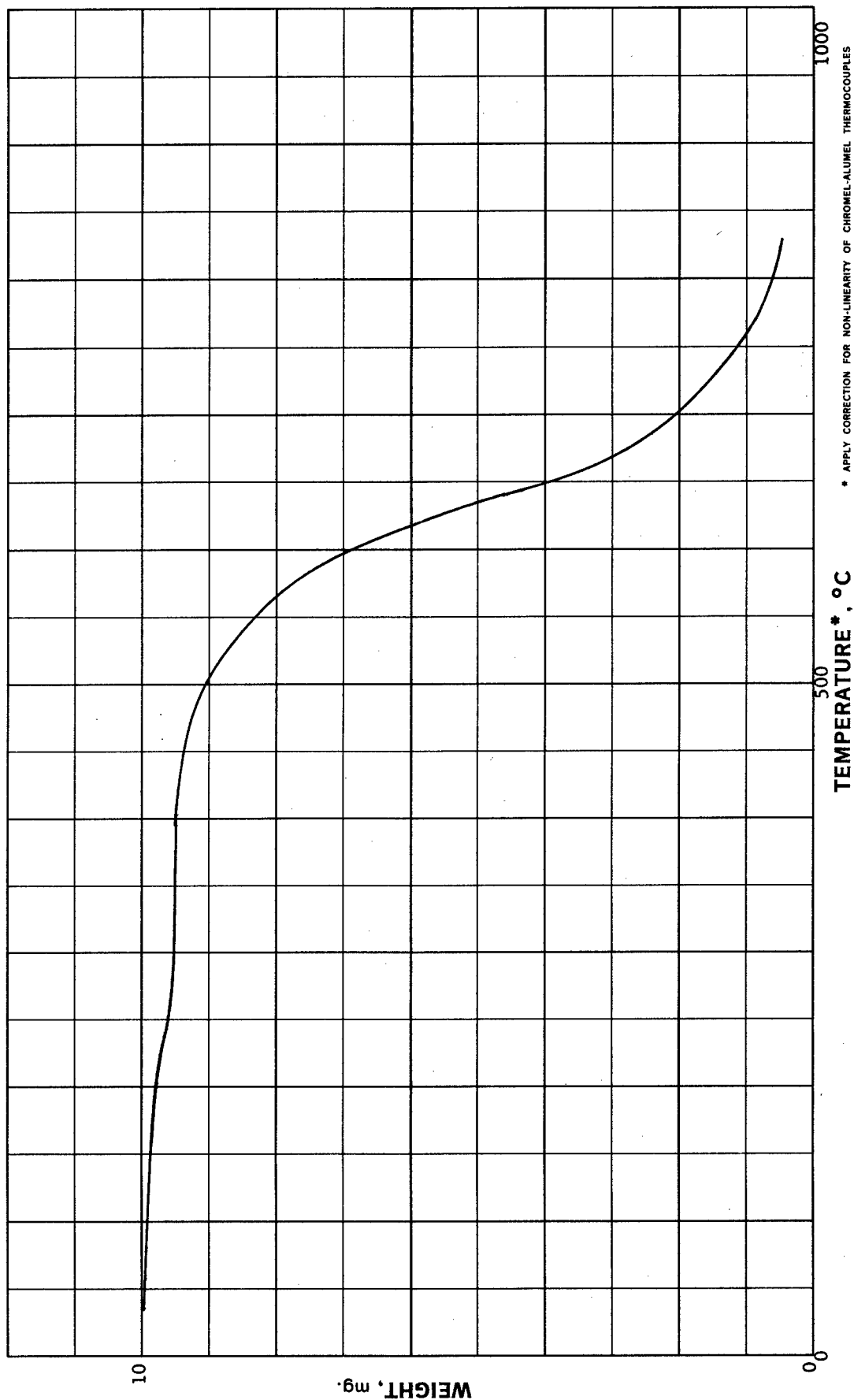
32

TEMPERATURE*, °C   * APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 9.   TGA in Air of BTPN-1.

33
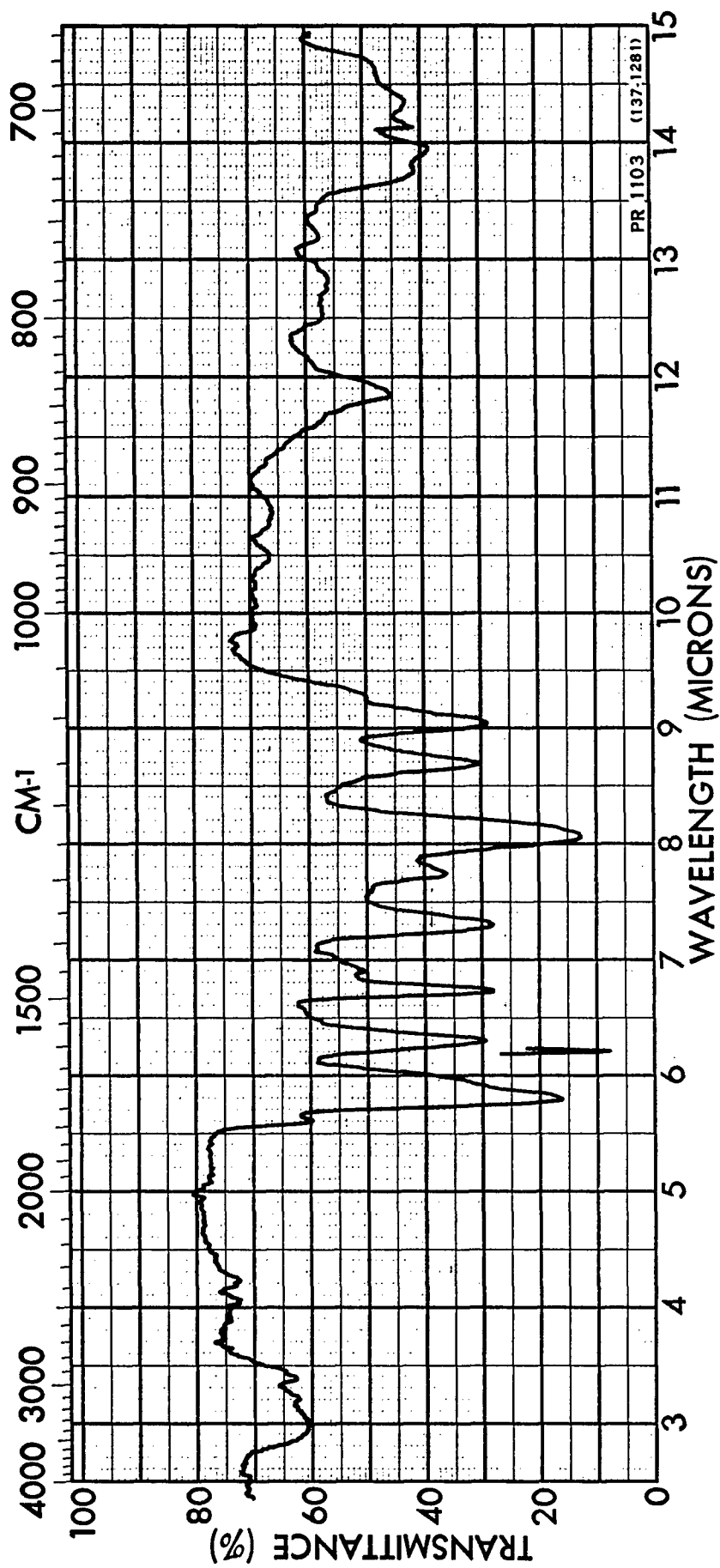
Figure 10.   Infrared Spectrum of BTAS-16 (KBr disc).

34
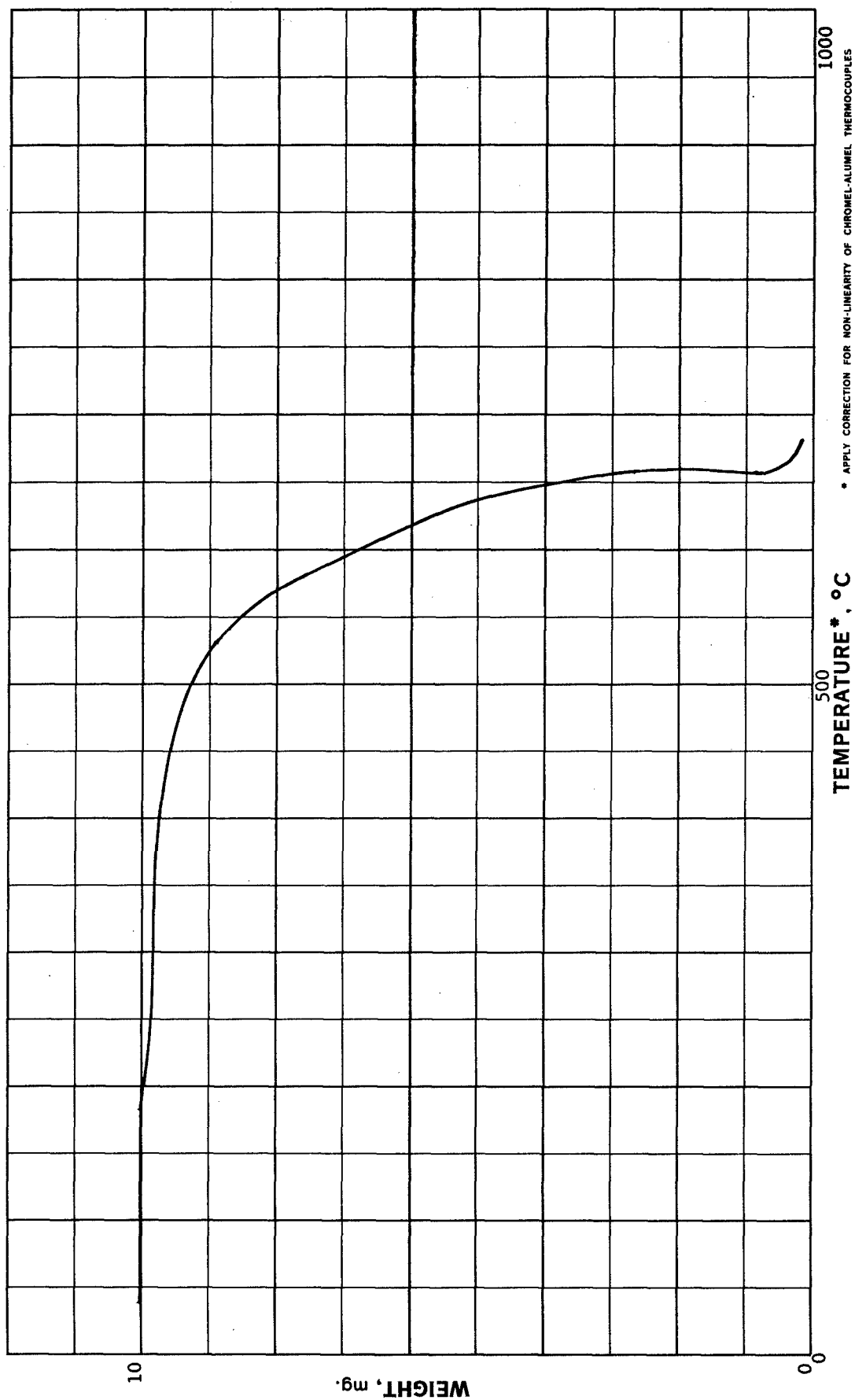
Figure 11. TGA in Air of BTAS-16.

35

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.
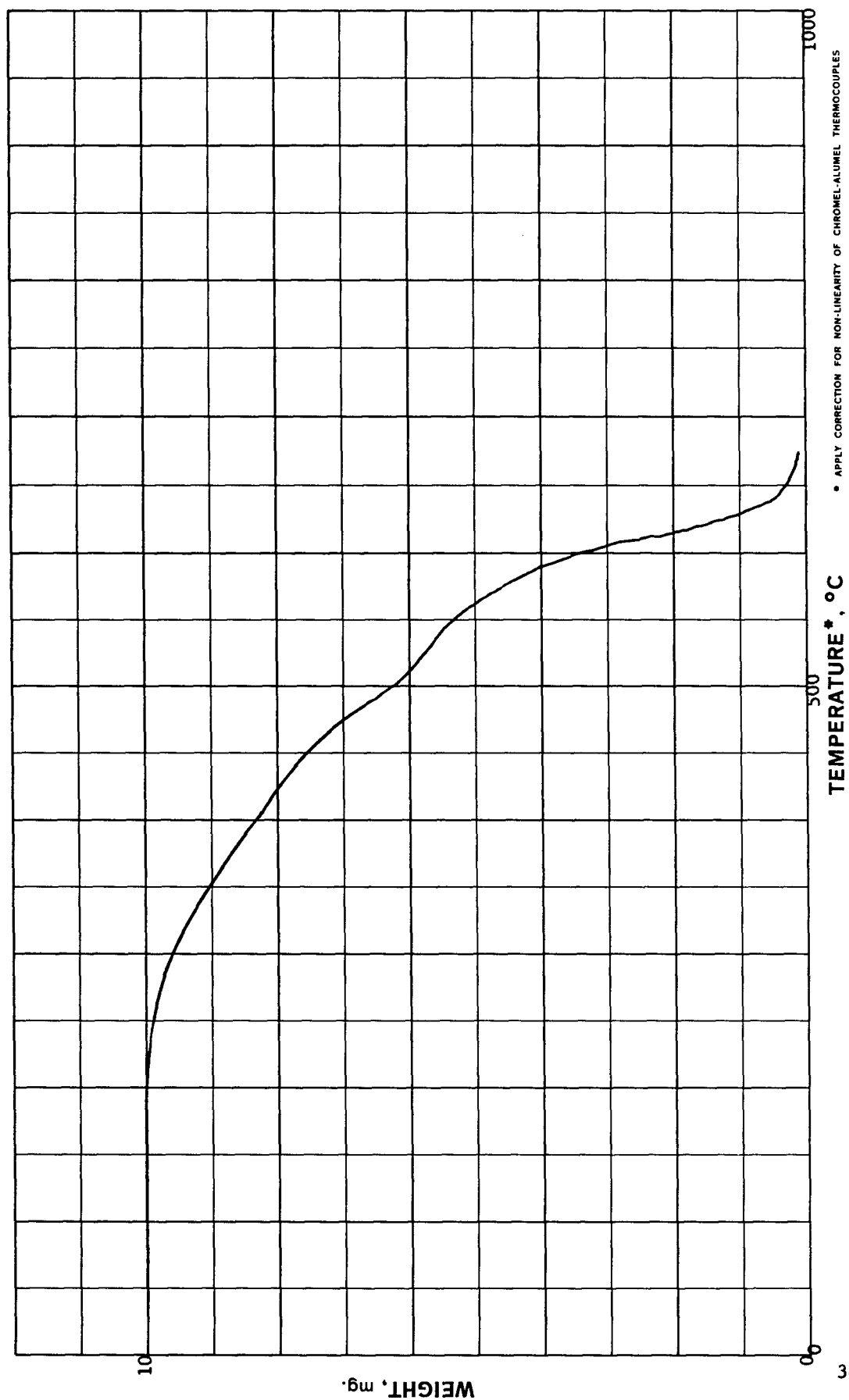
Figure 12.   TGA in Air of EP-1A-H300.
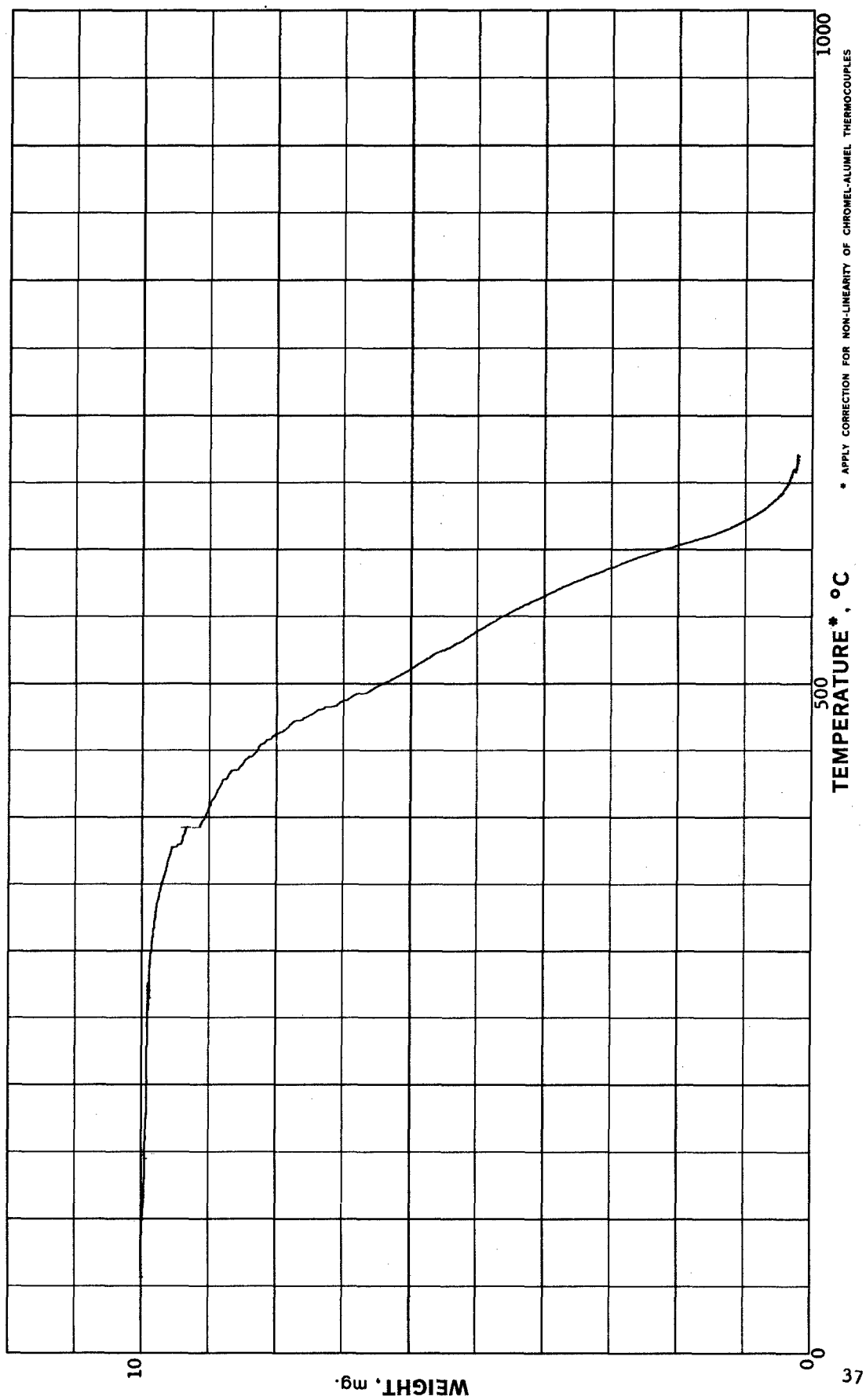
Figure 13. TGA in Air of EP-2A-H300.

TEMPERATURE*, °C

WEIGHT, mg.
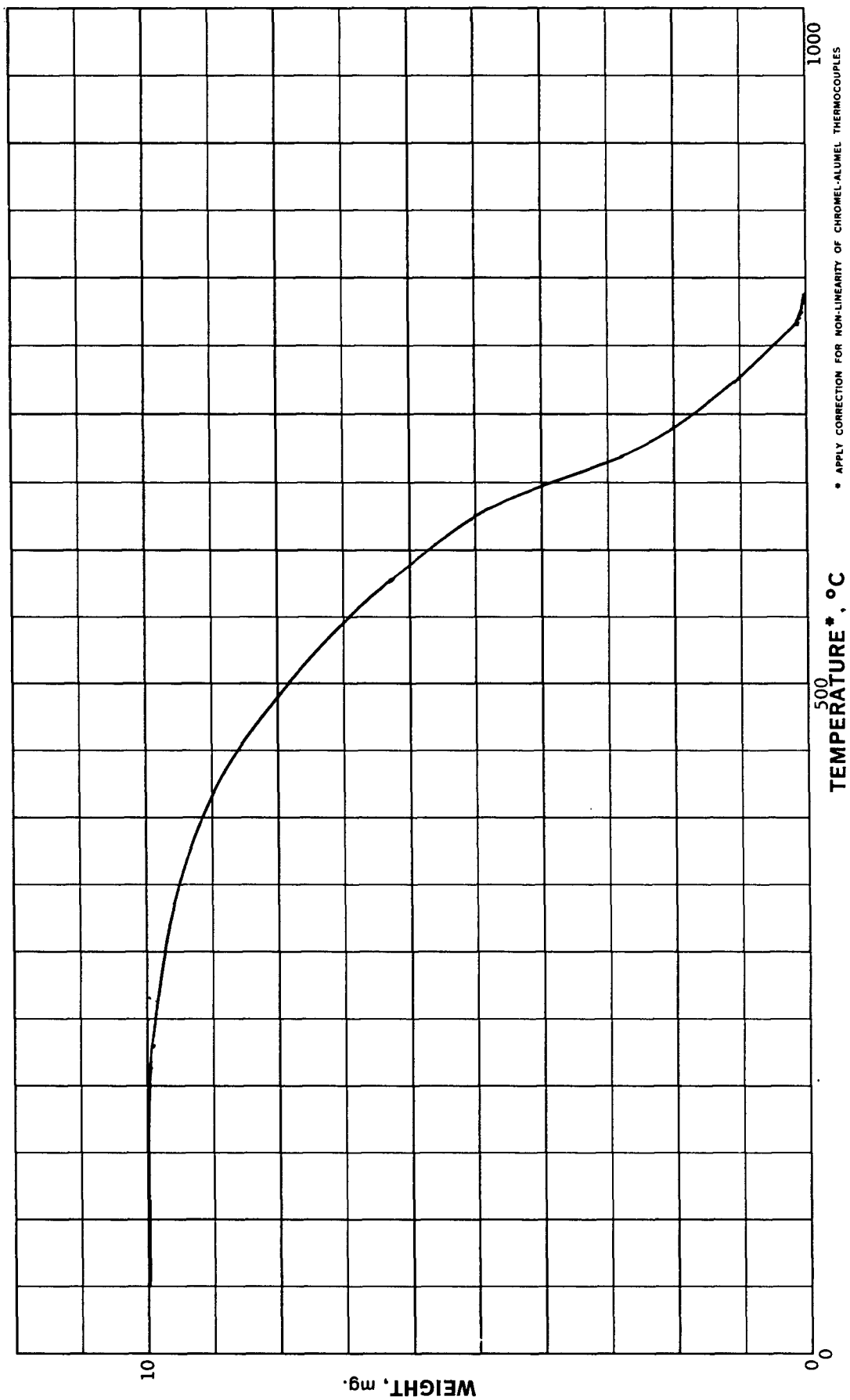
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

37
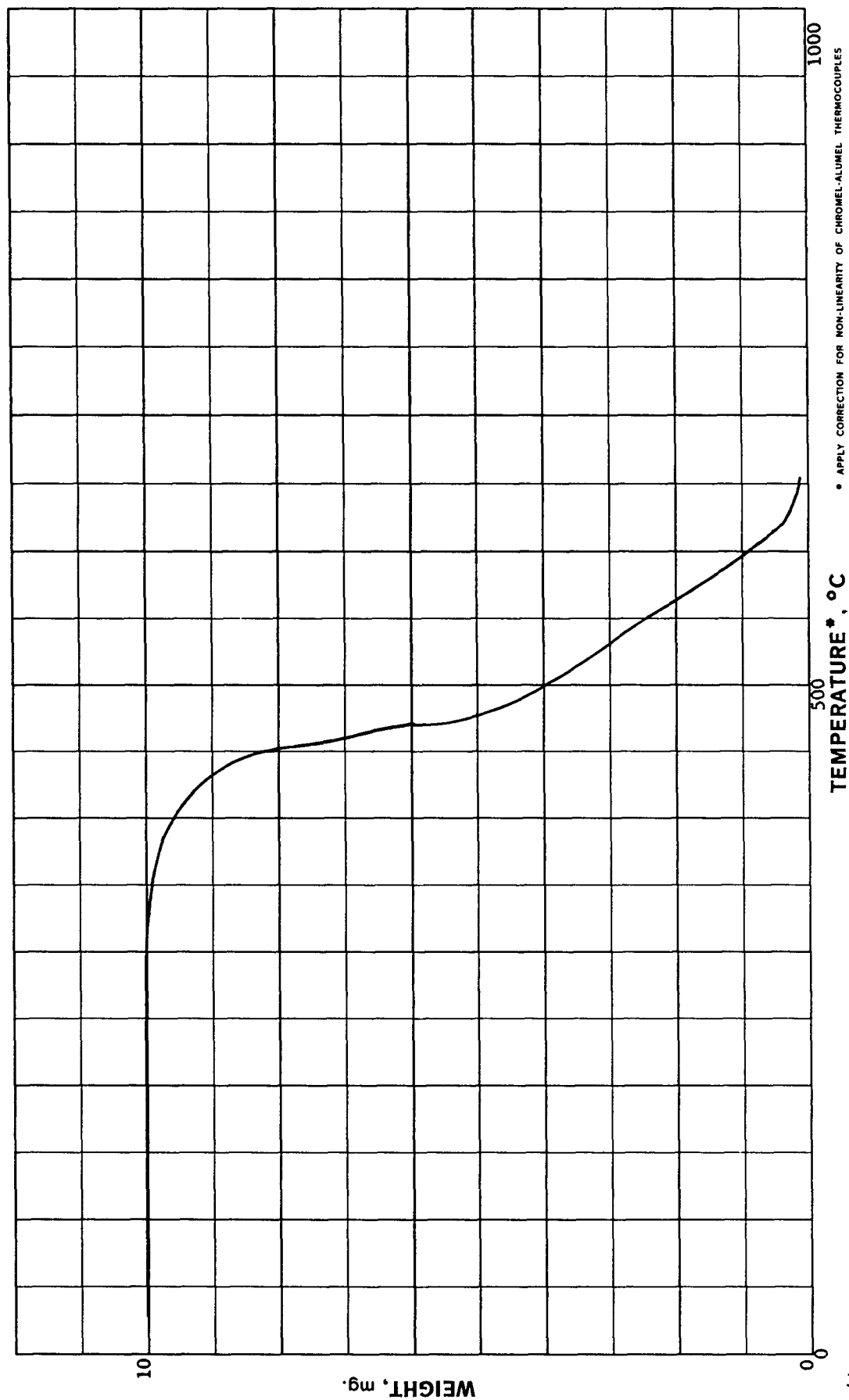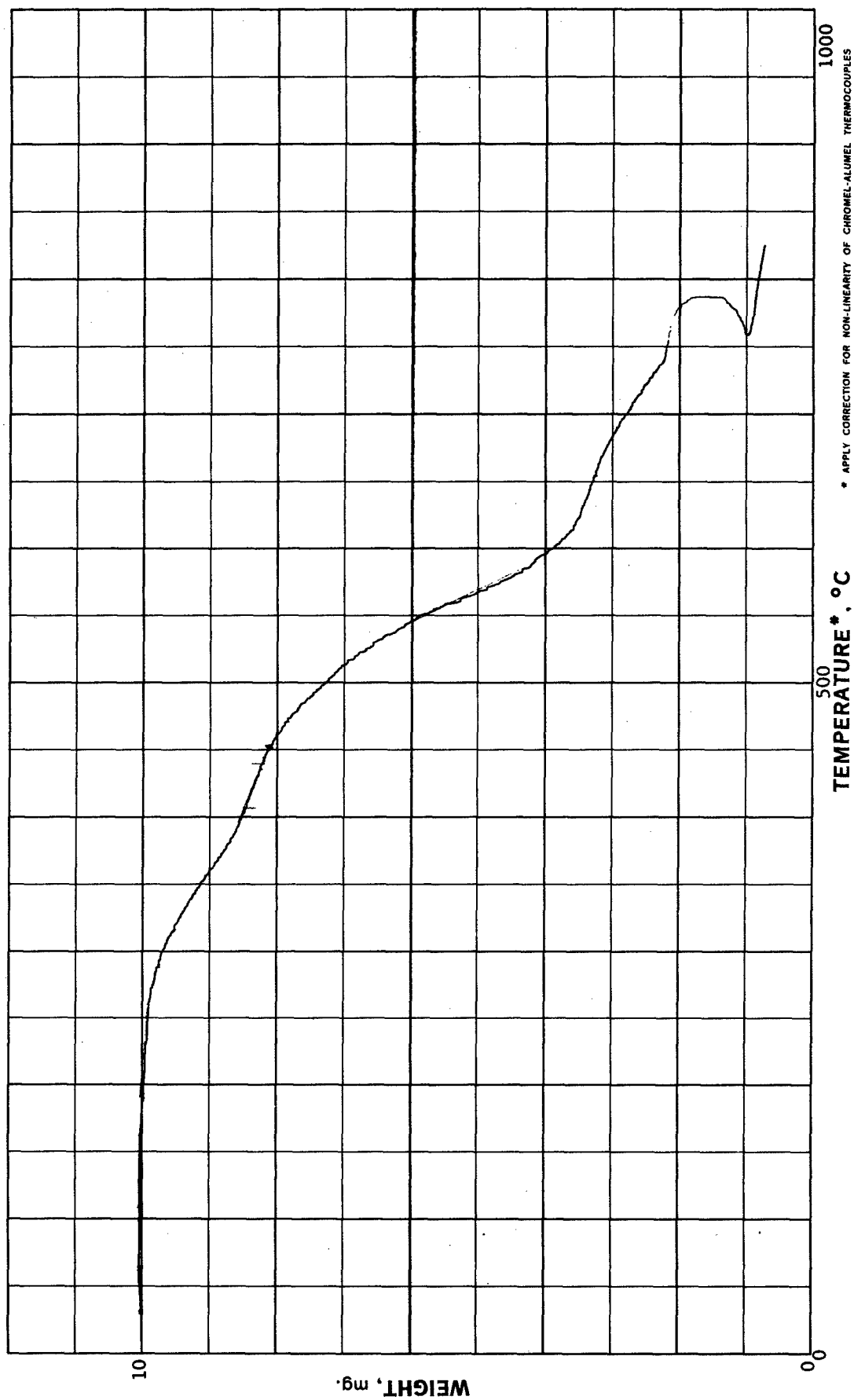
Figure 14. TGA in Air of EP-3A-H300.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE*, °C

WEIGHT, mg.

38
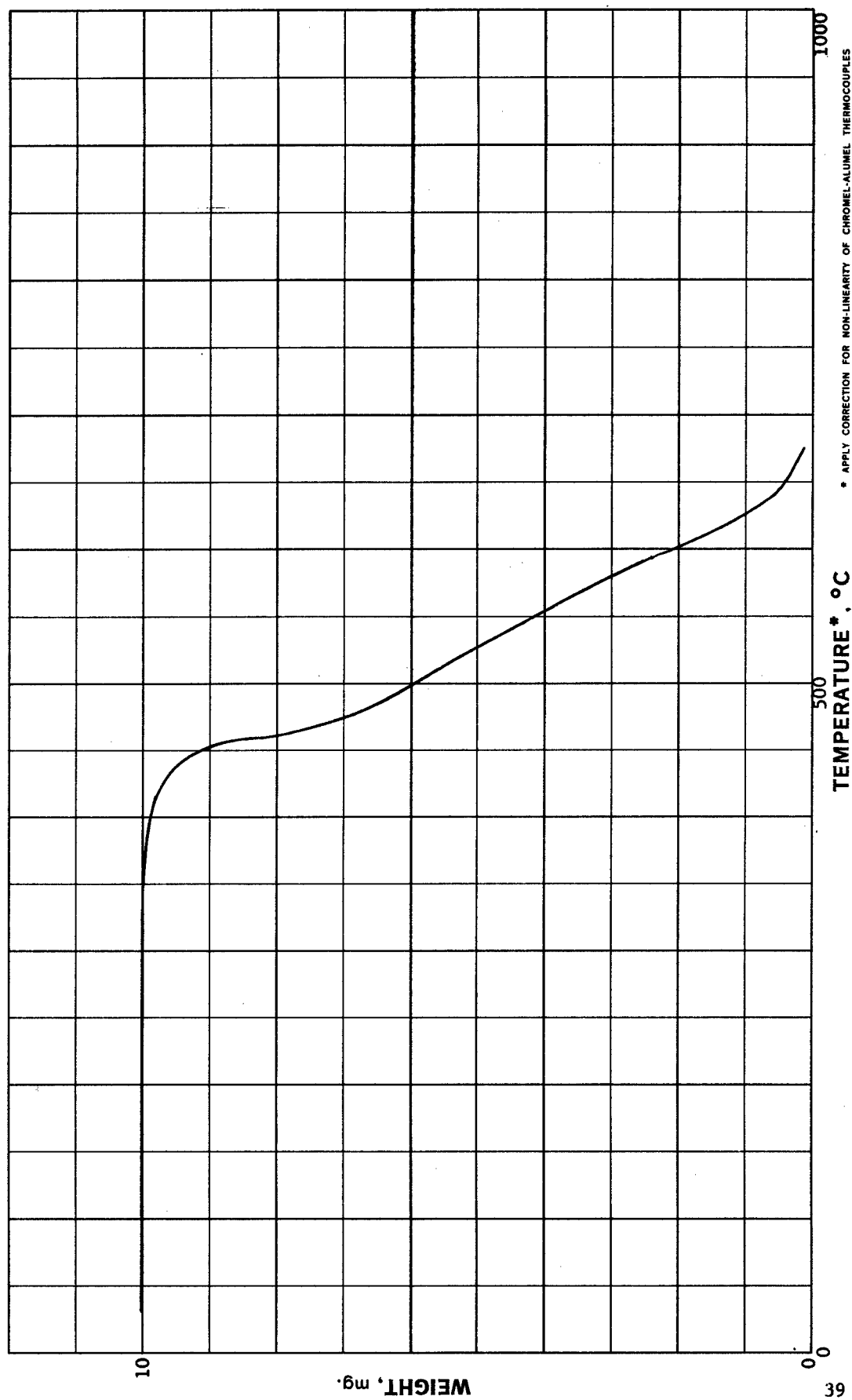
Figure 15.   TGA in Air of EP-4A-H300.
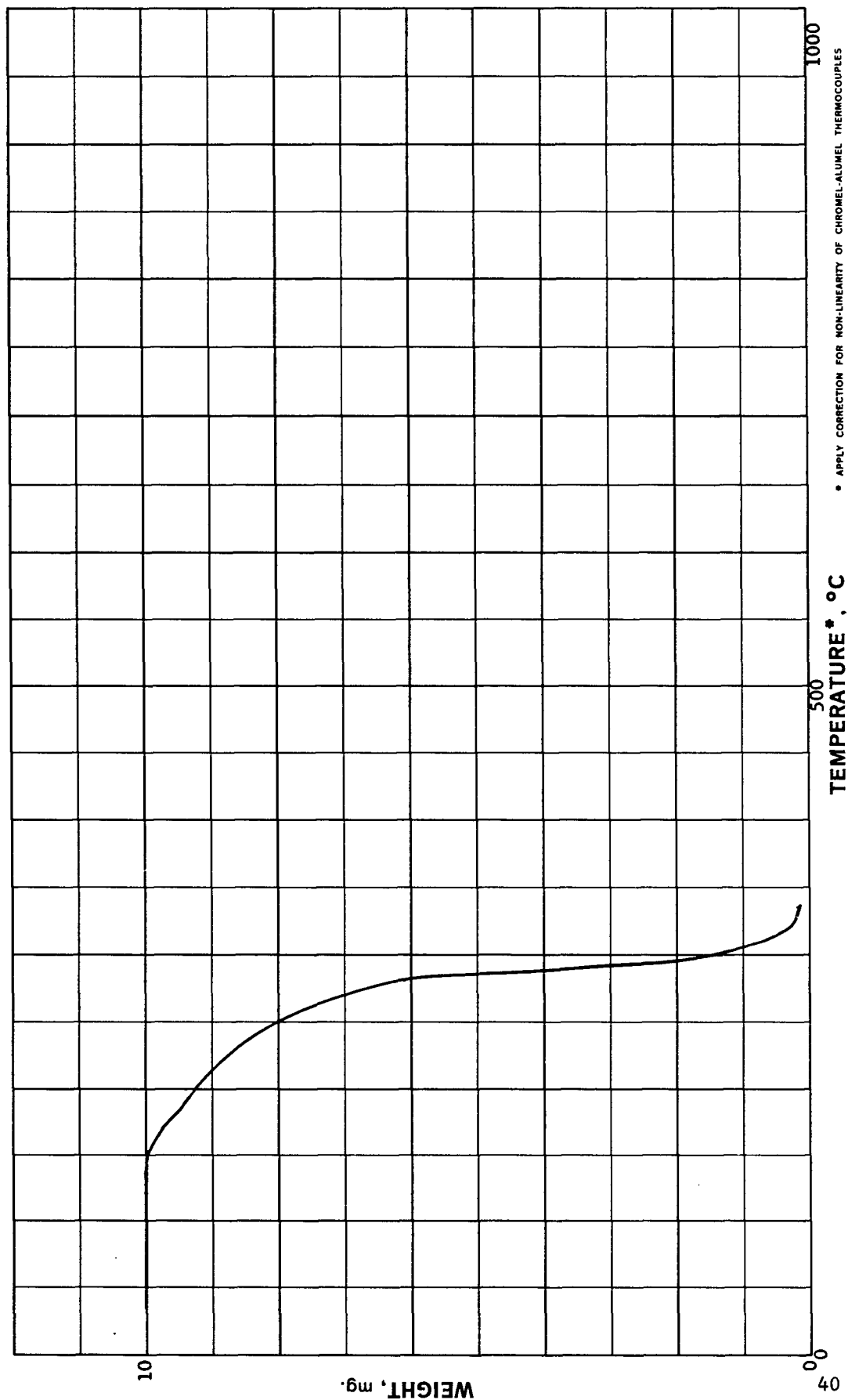
Figure 16. TGA in Air of ODA.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

0

500

1000

10

40

TEMPERATURE*, °C   * APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
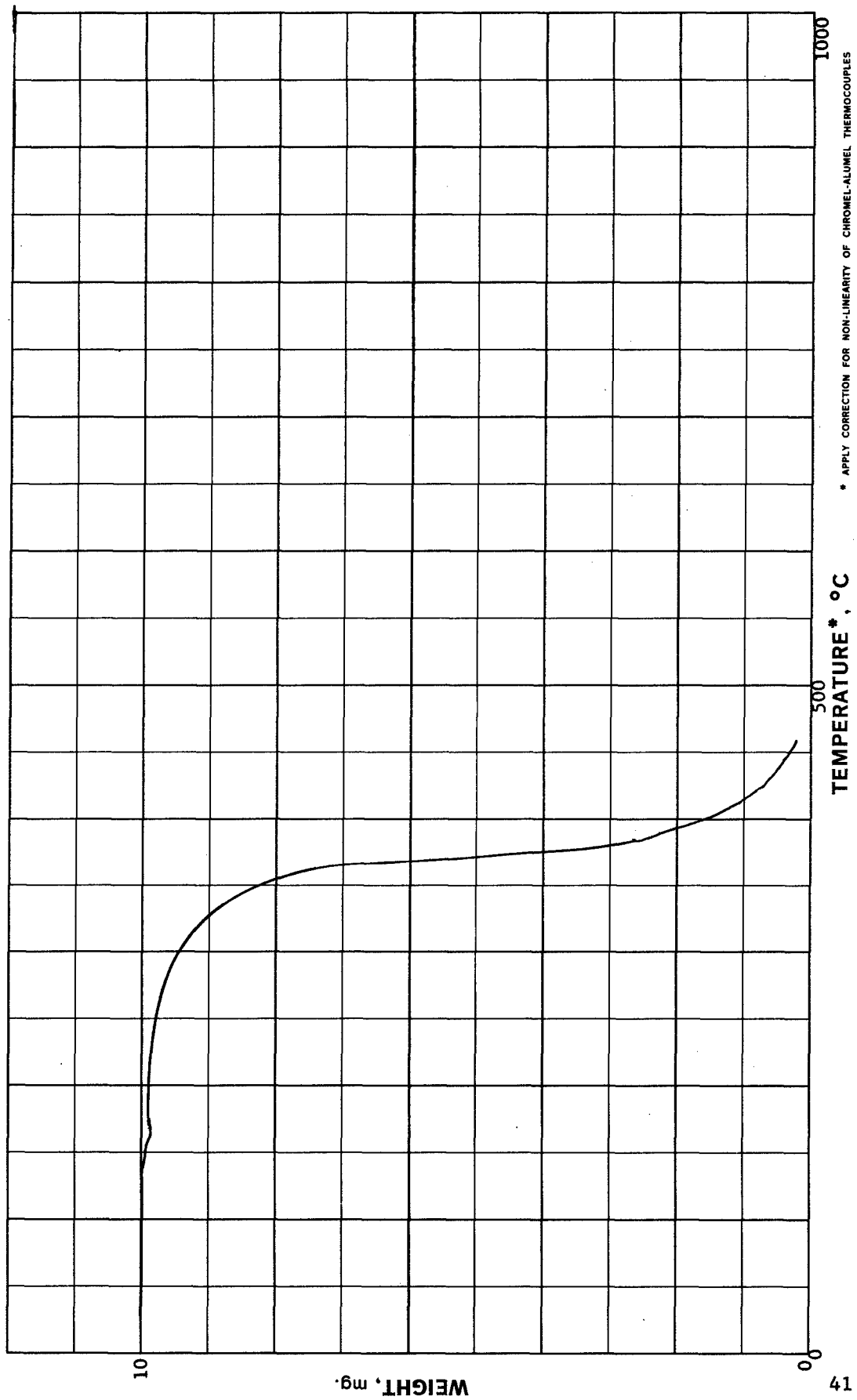
Figure 17. TGA in Air of DAPB-3,4.

41
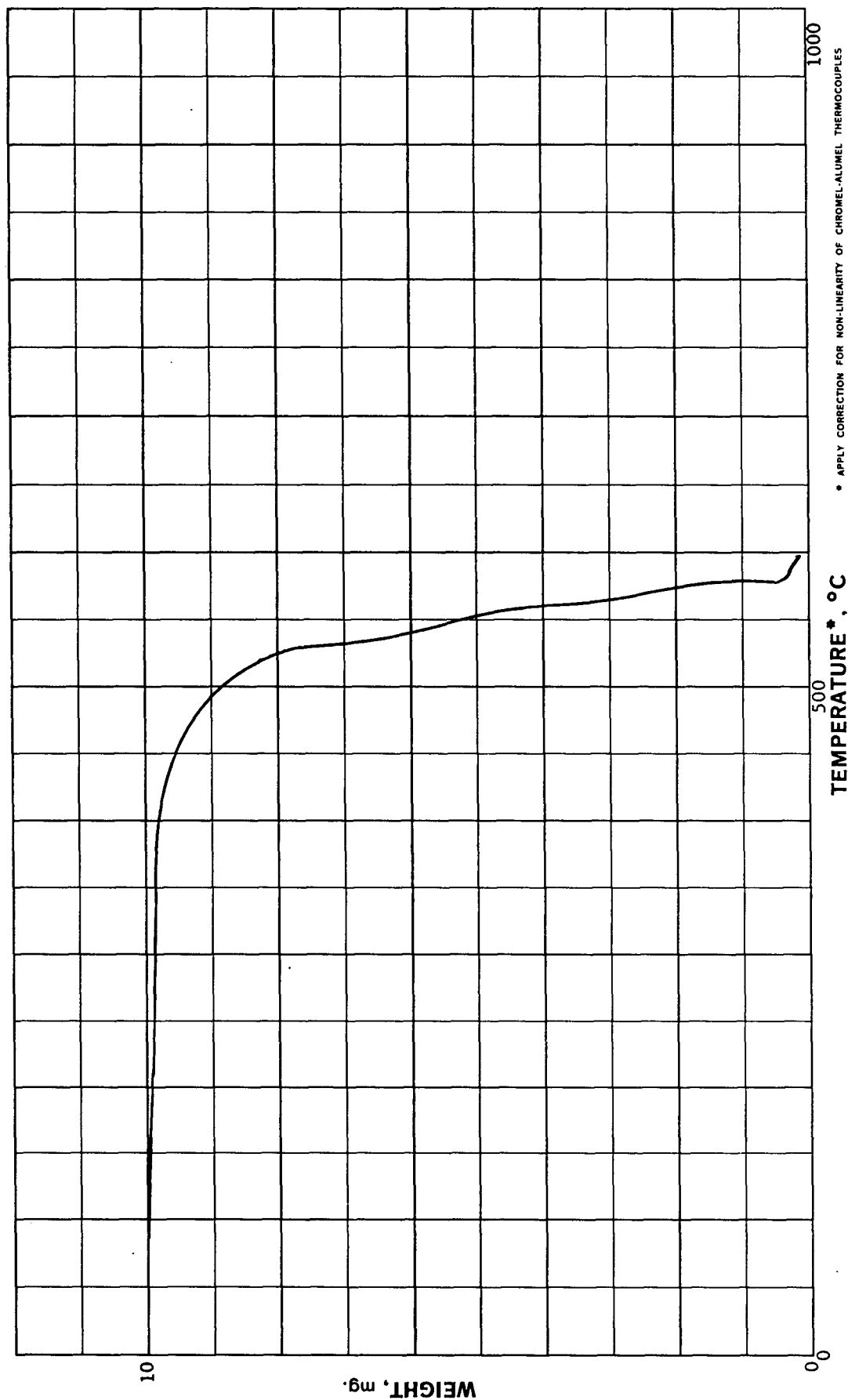
Figure 18.   TGA in Air of BTEP-4-H300.
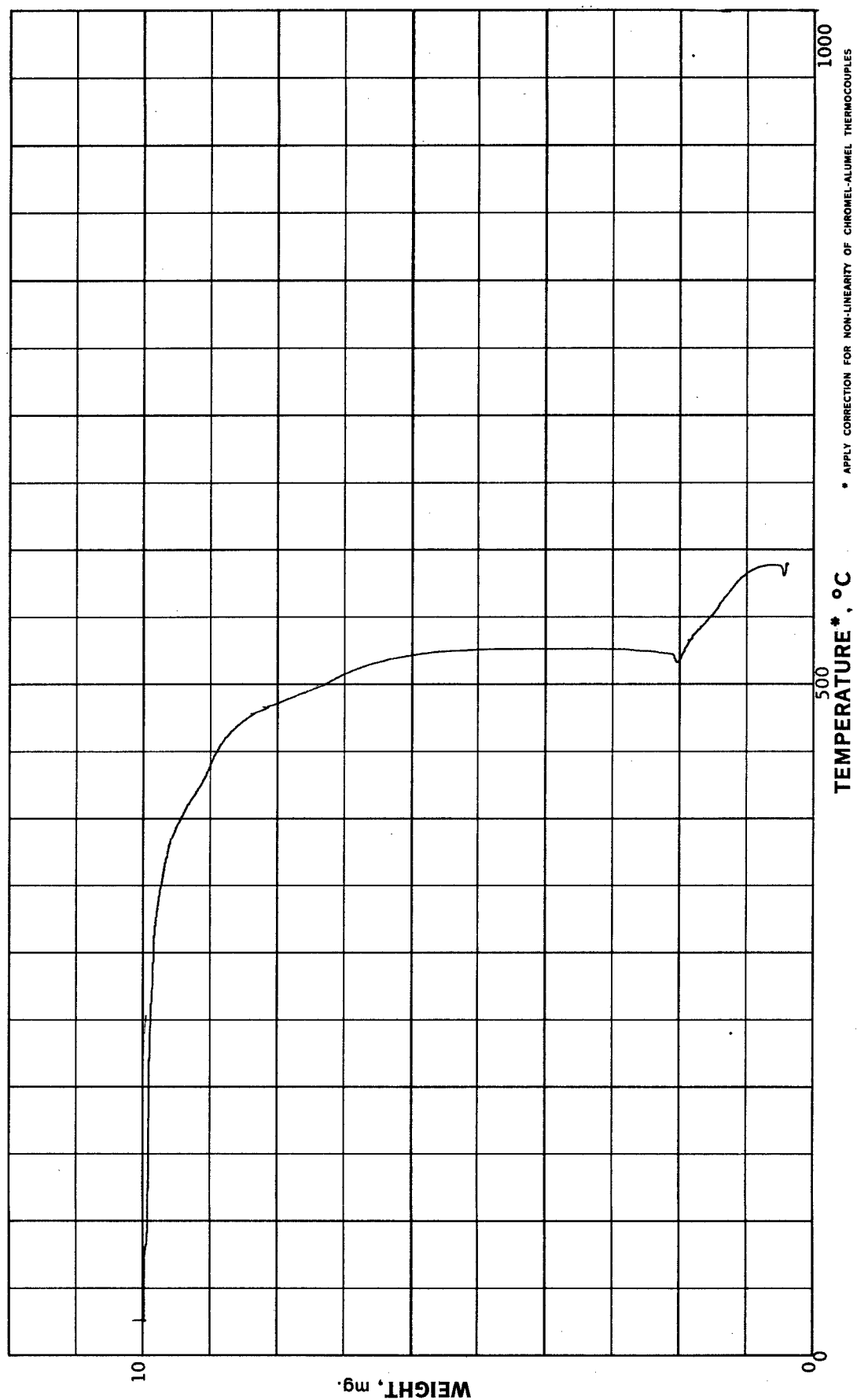
Figure 19. TGA in Air of BTEP-4 + PDA (1:1 mole) H250.
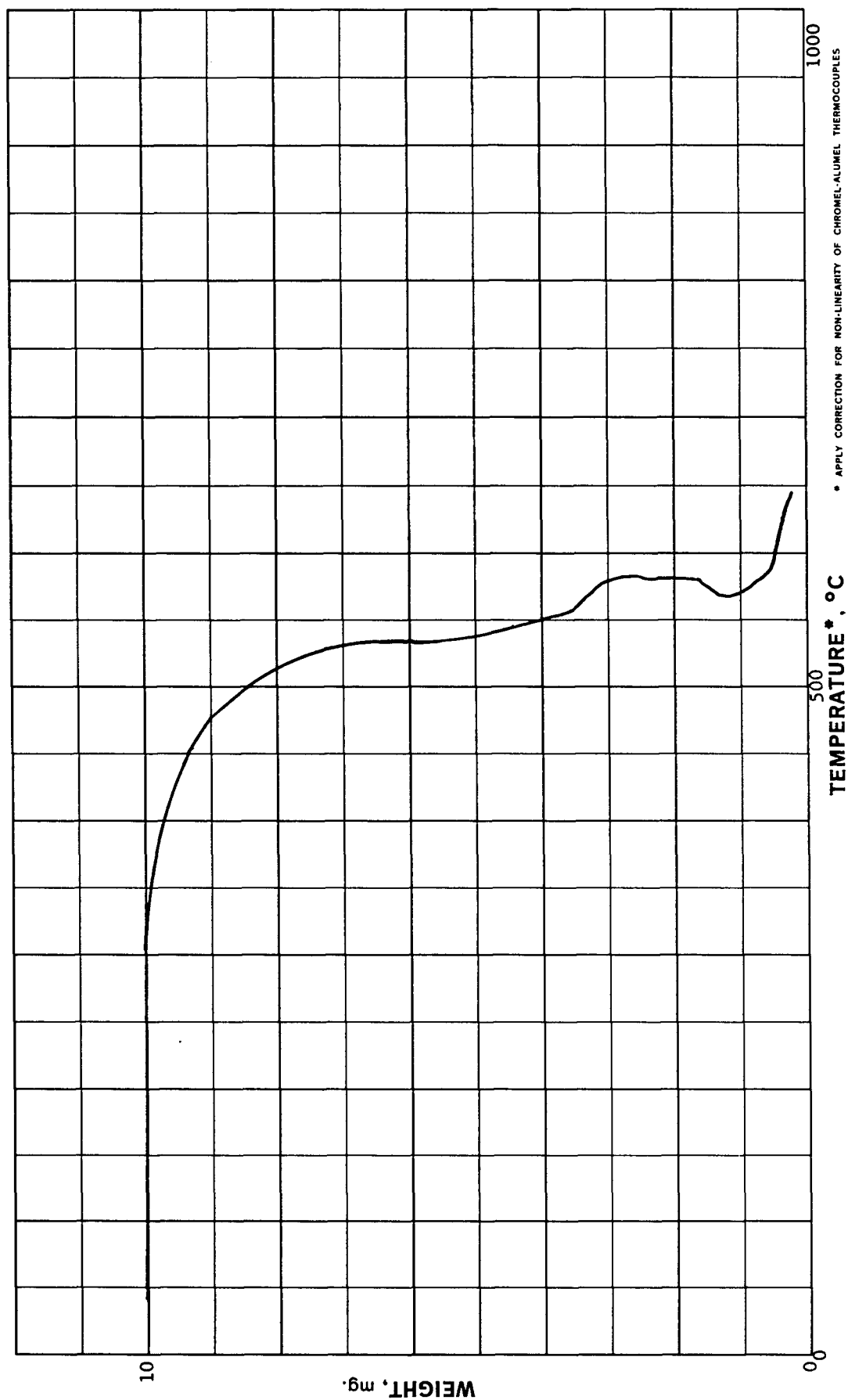
Figure 20.　TGA in Air of BTEP-5 H300.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE*, °C

WEIGHT, mg.
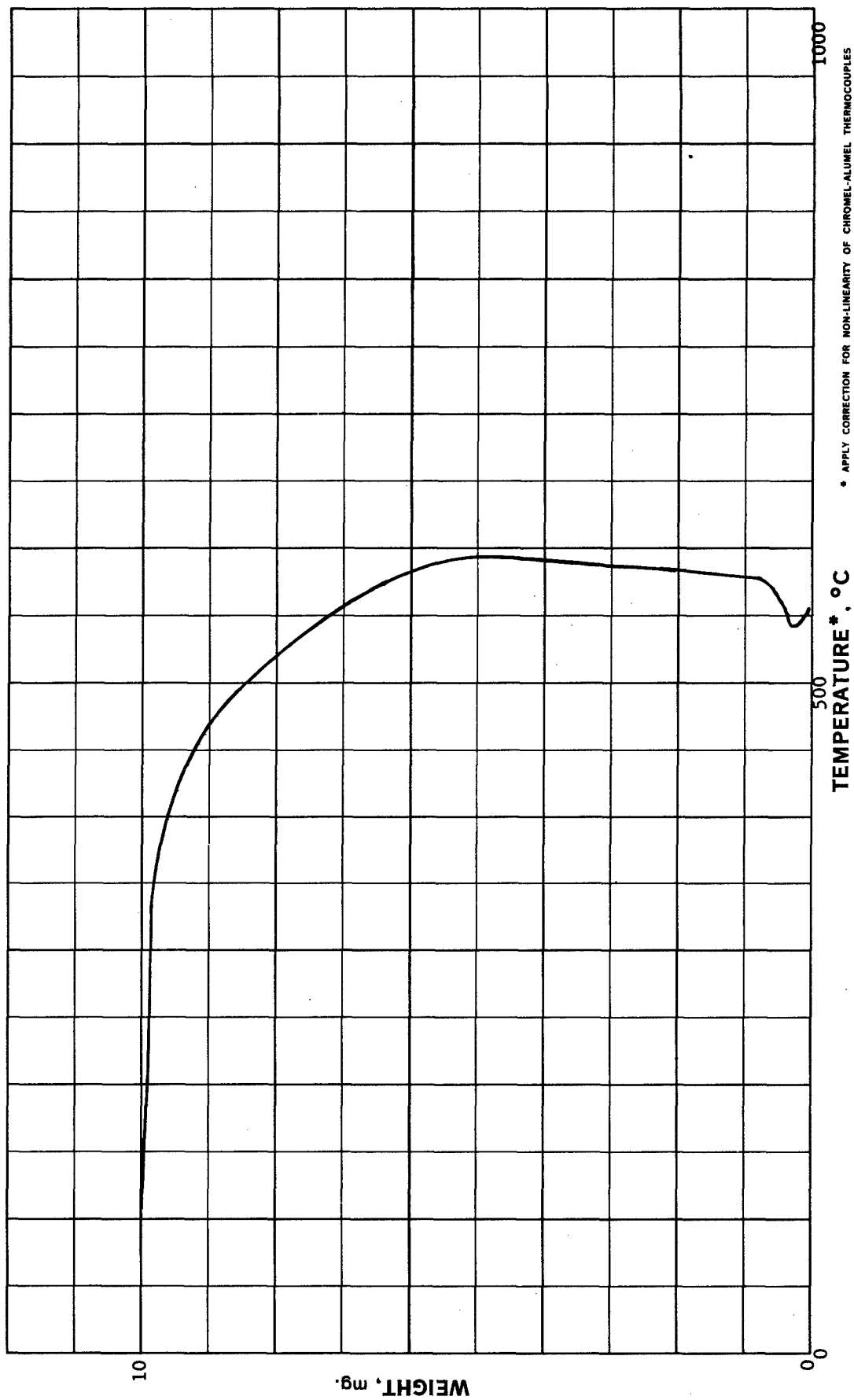
TEMPERATURE*, °C   * APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 21.   TGA in Air of BTEP-5 + 5% w/w DMP-30 H300.

45
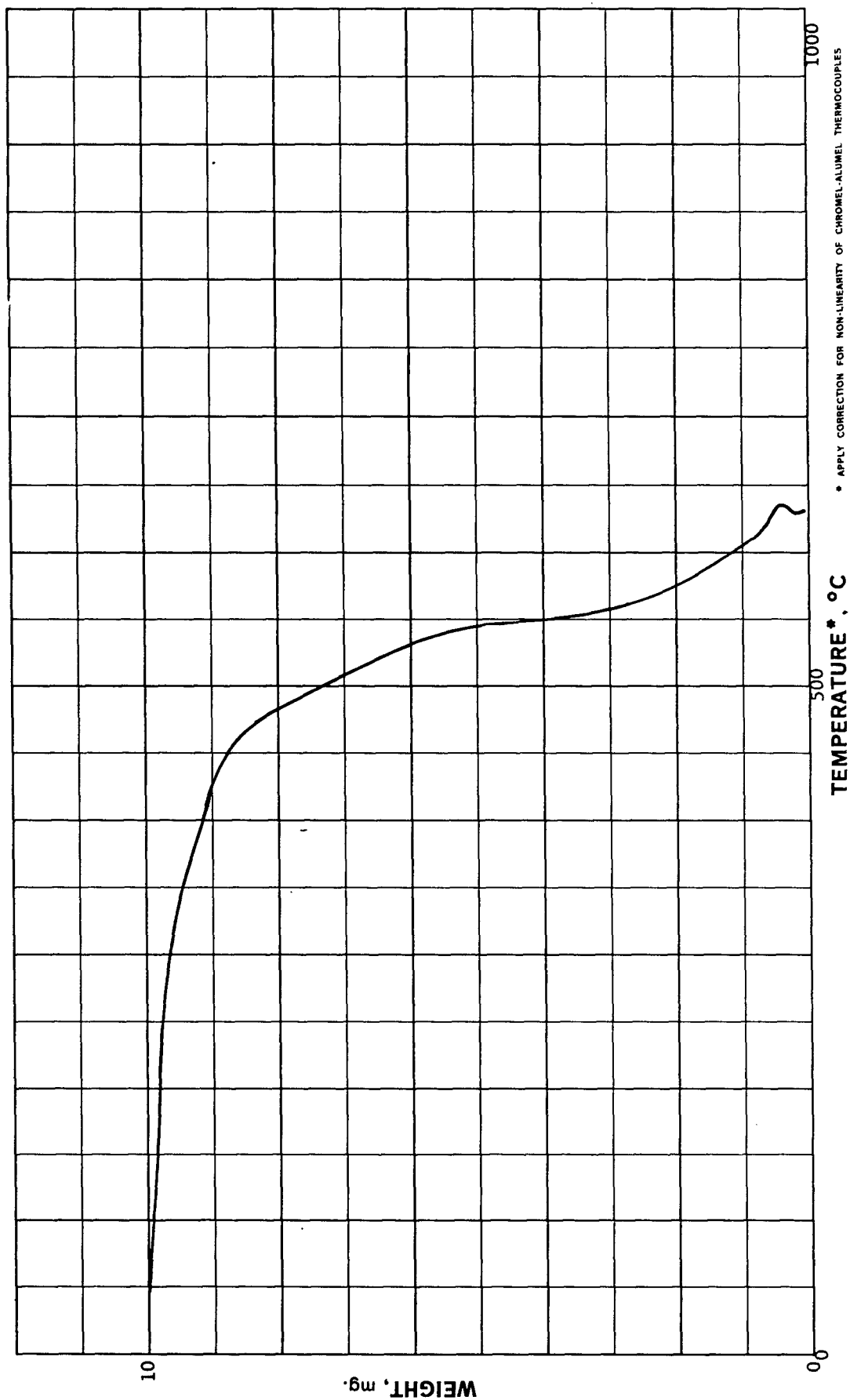
Figure 22. TGA in Air of BTEP-5 + m-PDA (1:2 mole) H250.
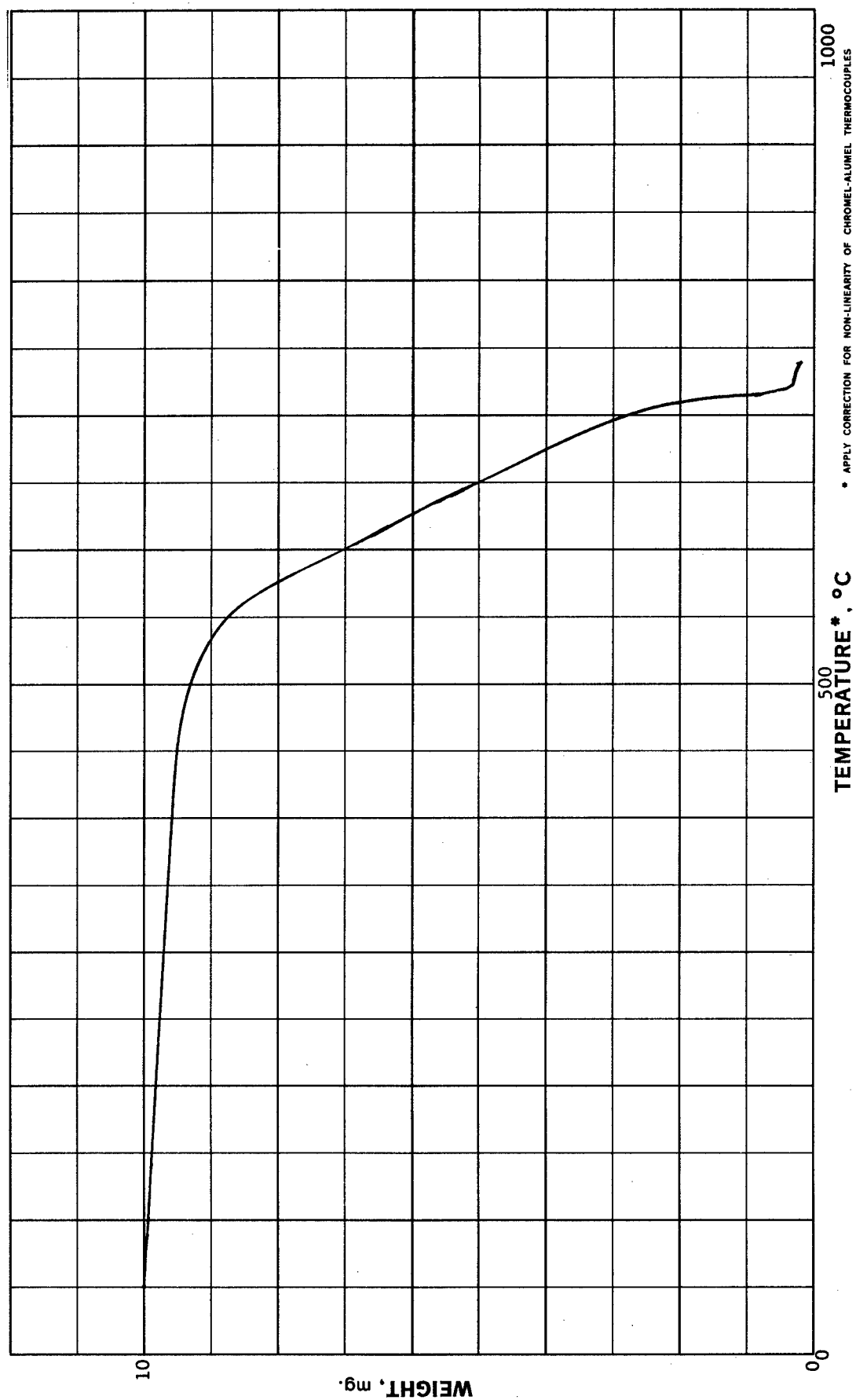
TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
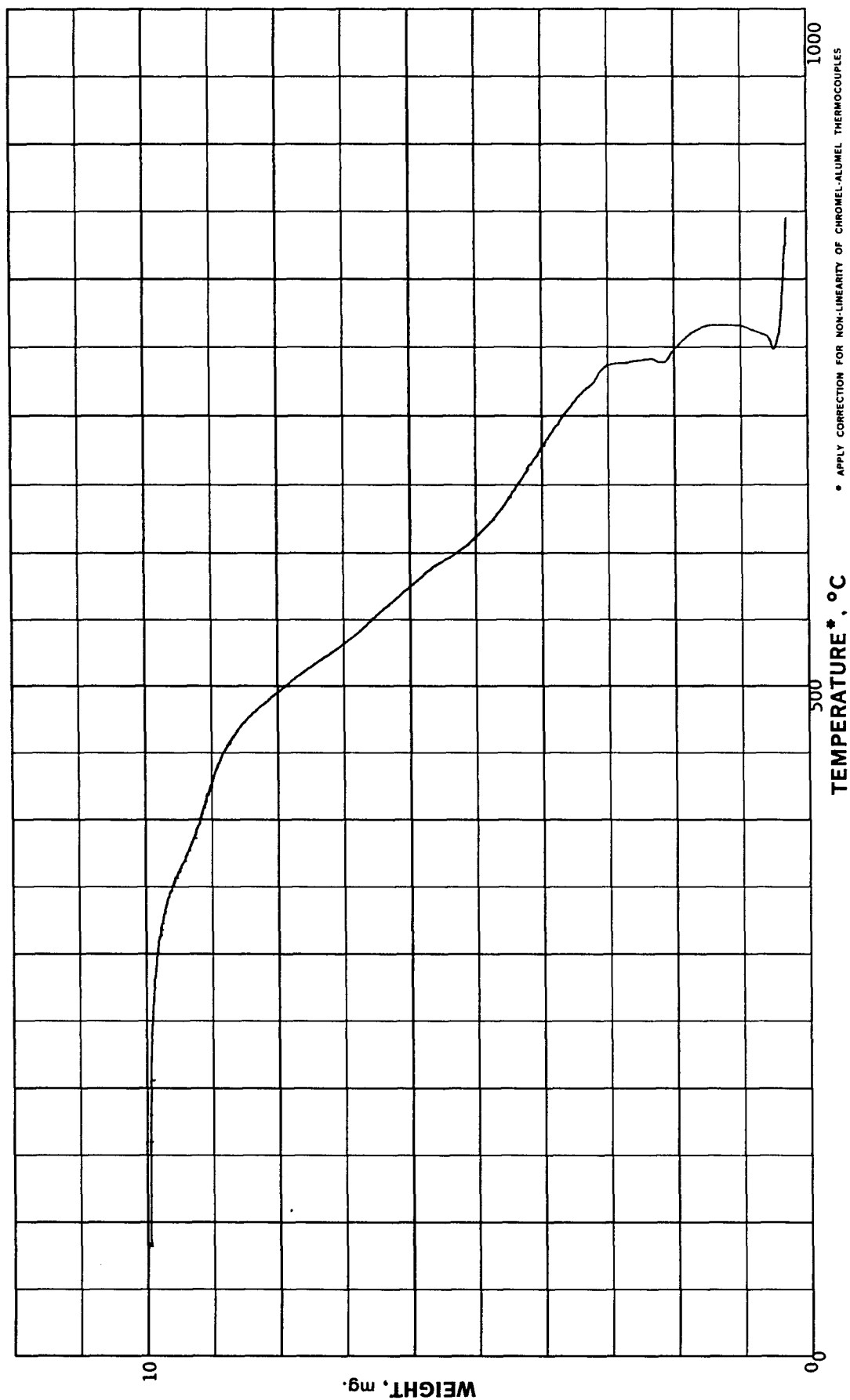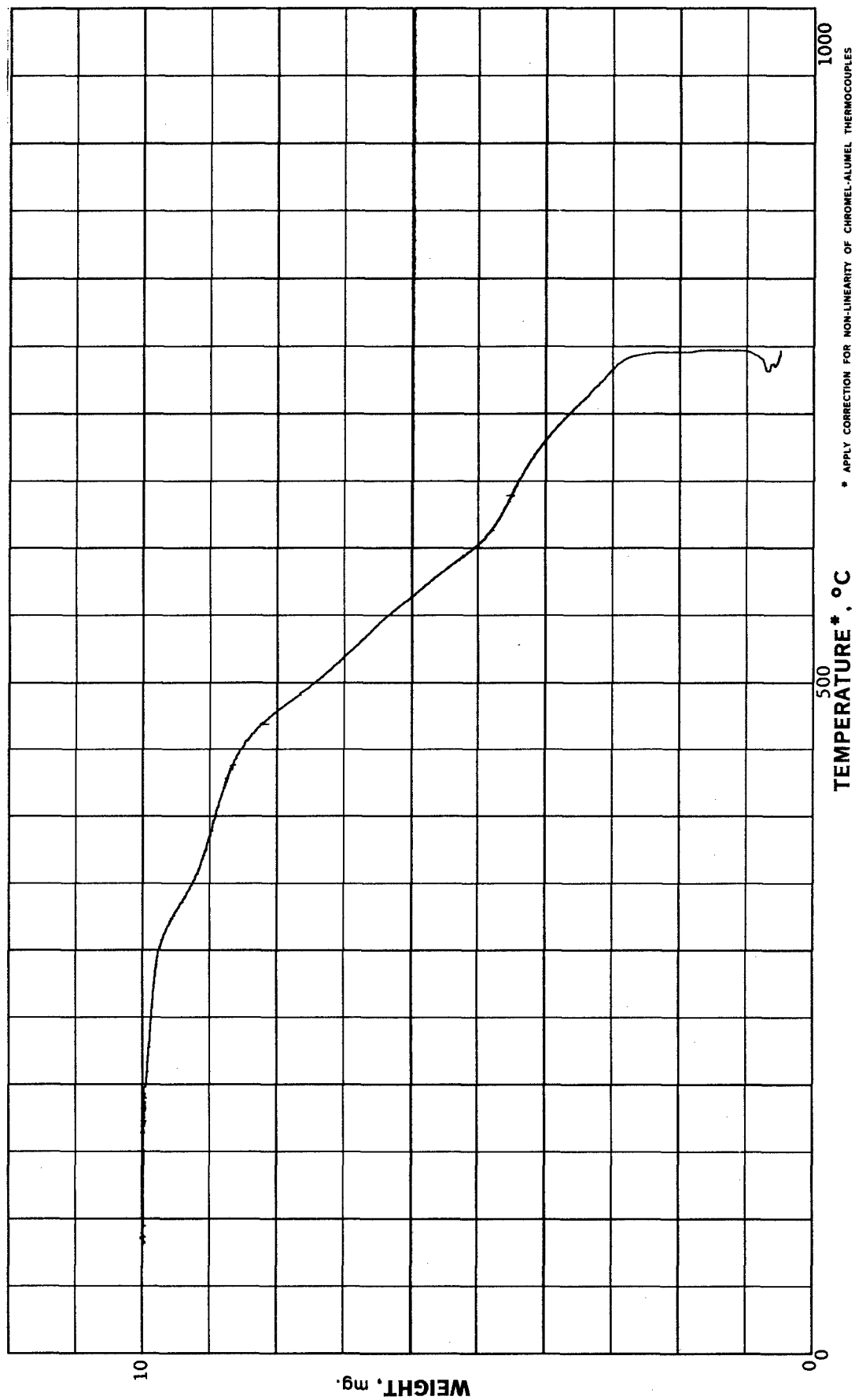
WEIGHT, mg.

Figure 23. TGA in Air of BTEP-6 + m-PDA (1:1 mole) H225.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

47
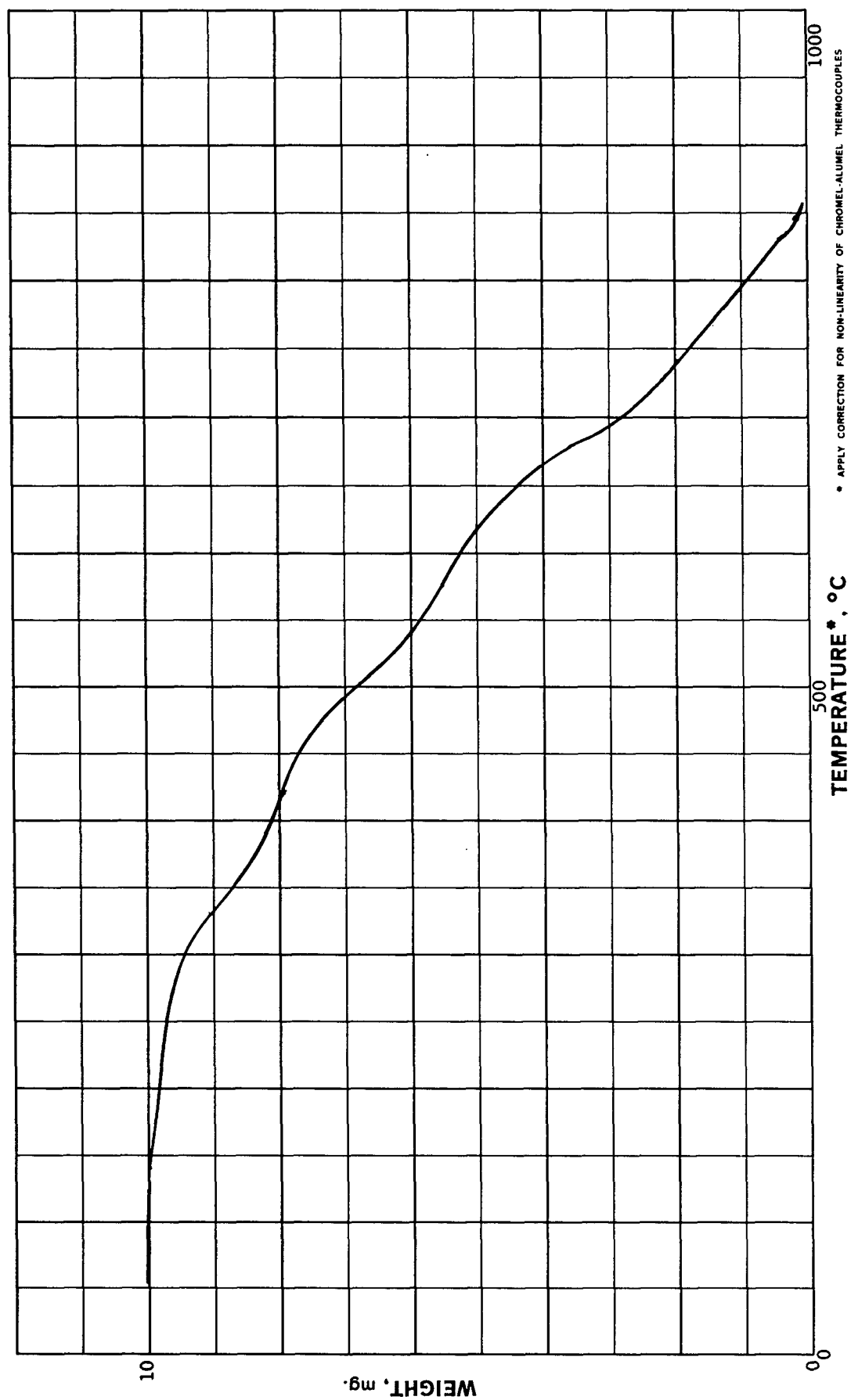
Figure 24.   TGA in Air of BTEP-7 + m-PDA (1:1 mole) H225.
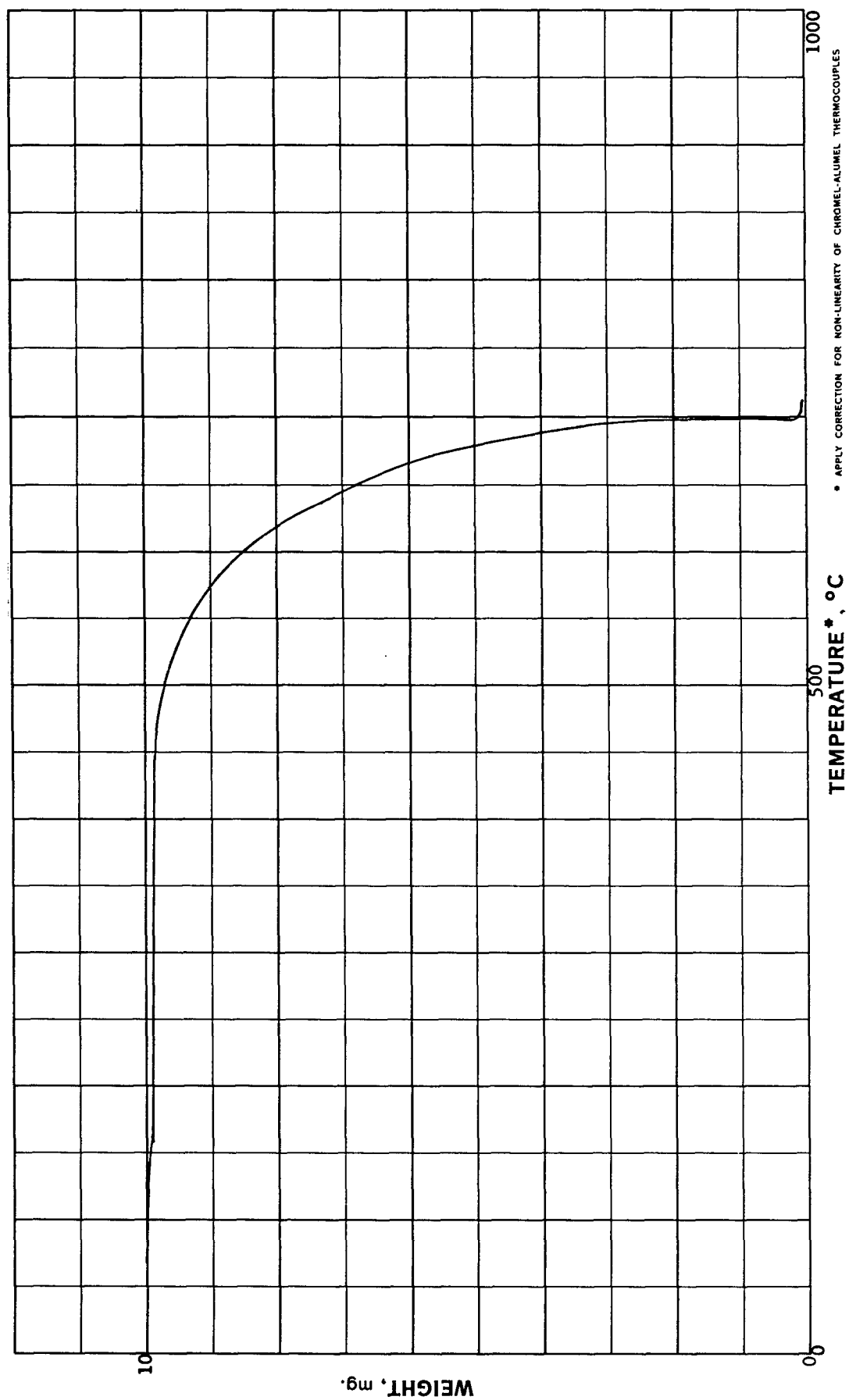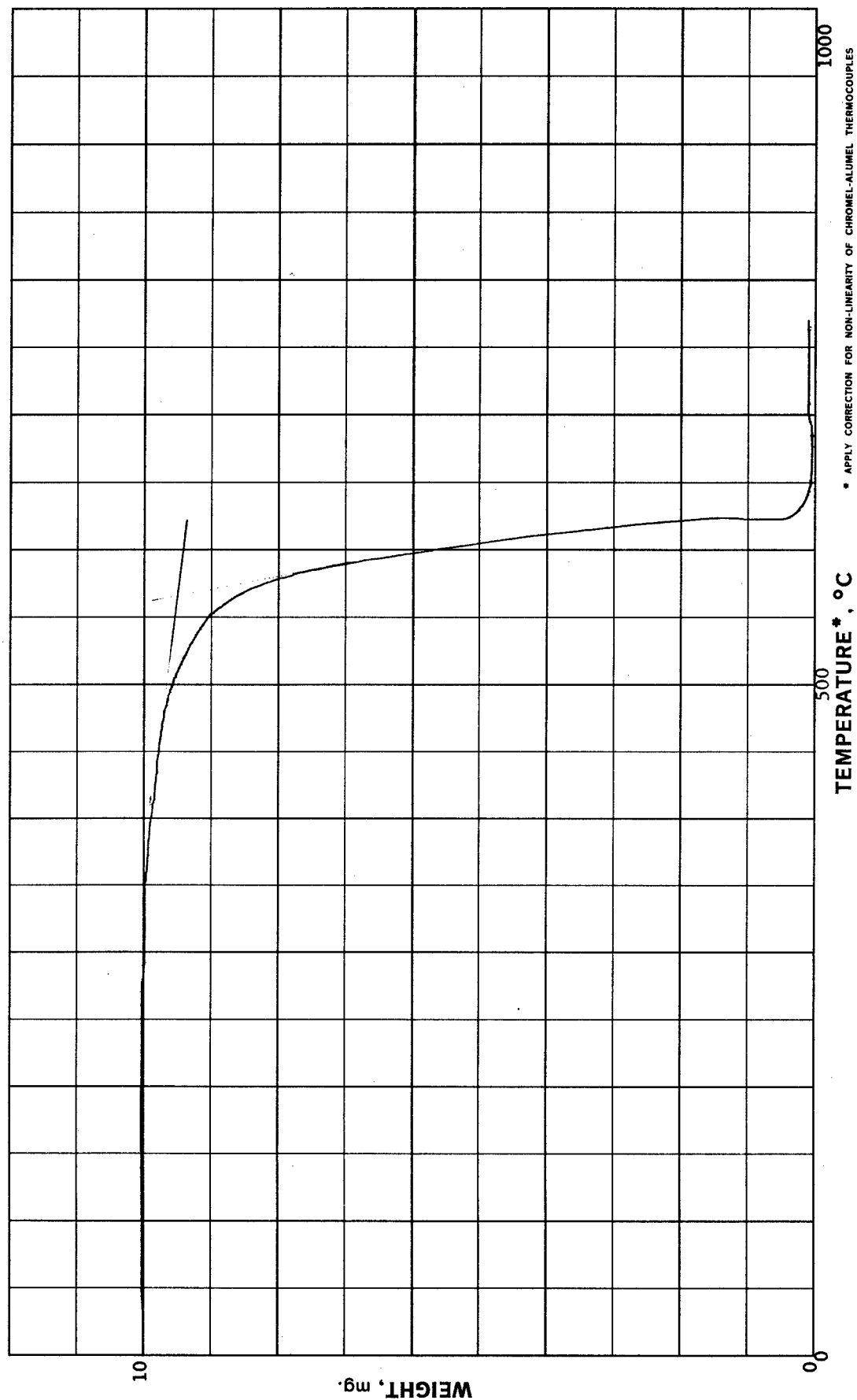
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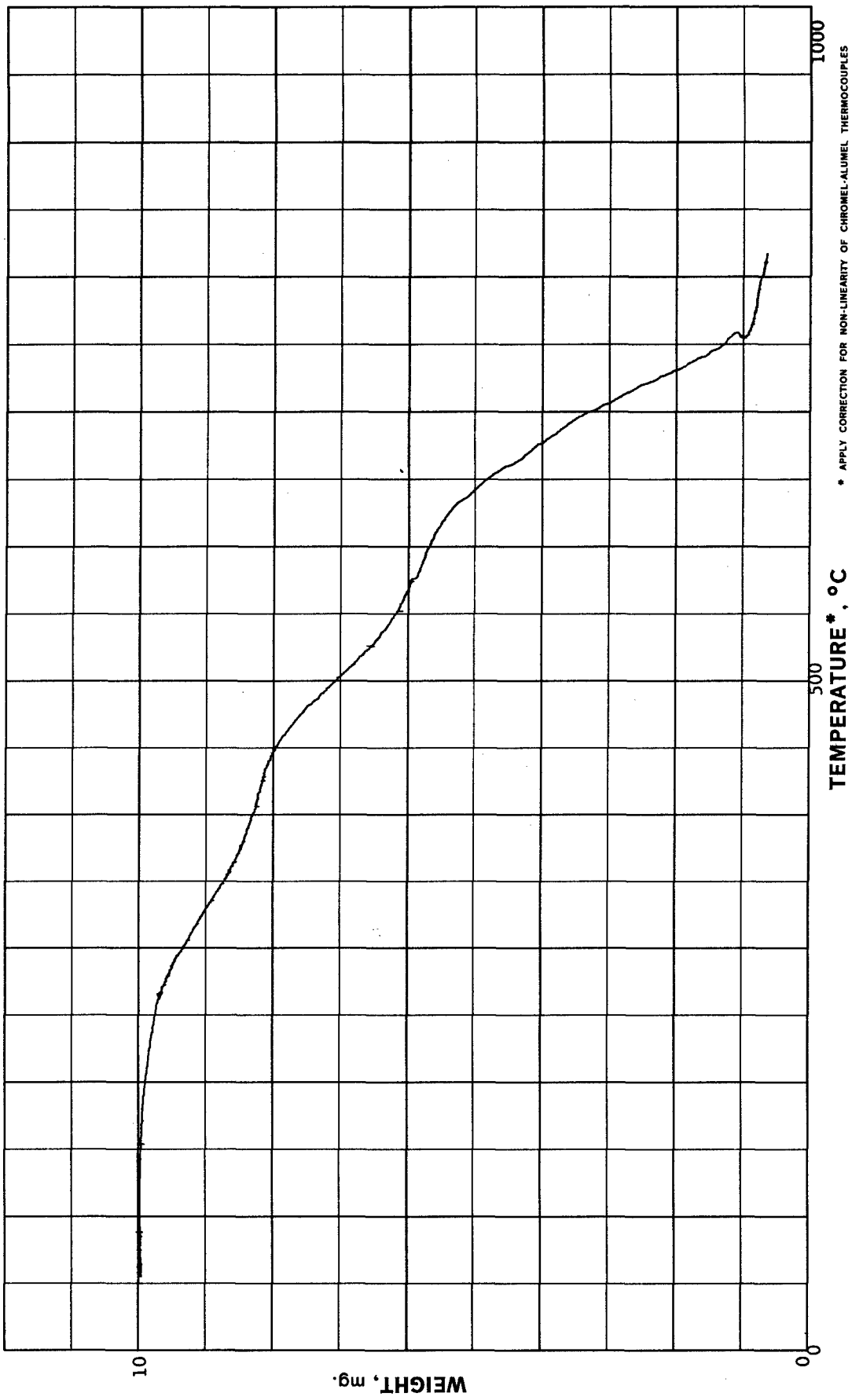
Figure 25. TGA in Air of BTEP-7 + PDA (1:2 mole) H250.

TEMPERATURE*, °C   * APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

49

Figure 26. TGA in Air of BTEP-7 + 5% w/w Bz₃N (225.

Figure 27. TGA in Air of BTEP-8 + PDA (1:1 mole) H225.
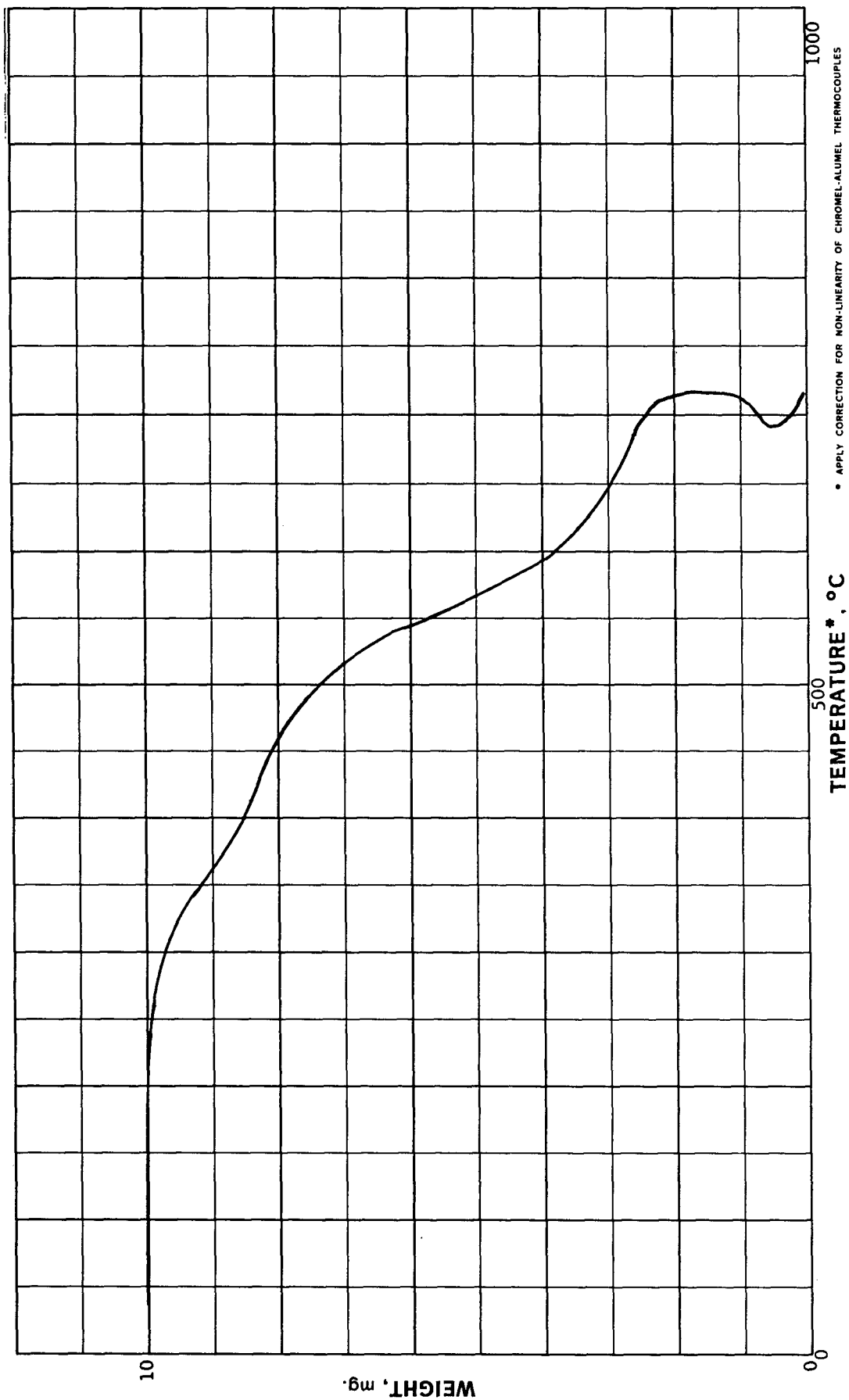
Figure 28. TGA in Air of BTEP-8 + PDA (1:2 mole) H250.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

52

WEIGHT, mg.

10

0

500 1000

TEMPERATURE*, °C
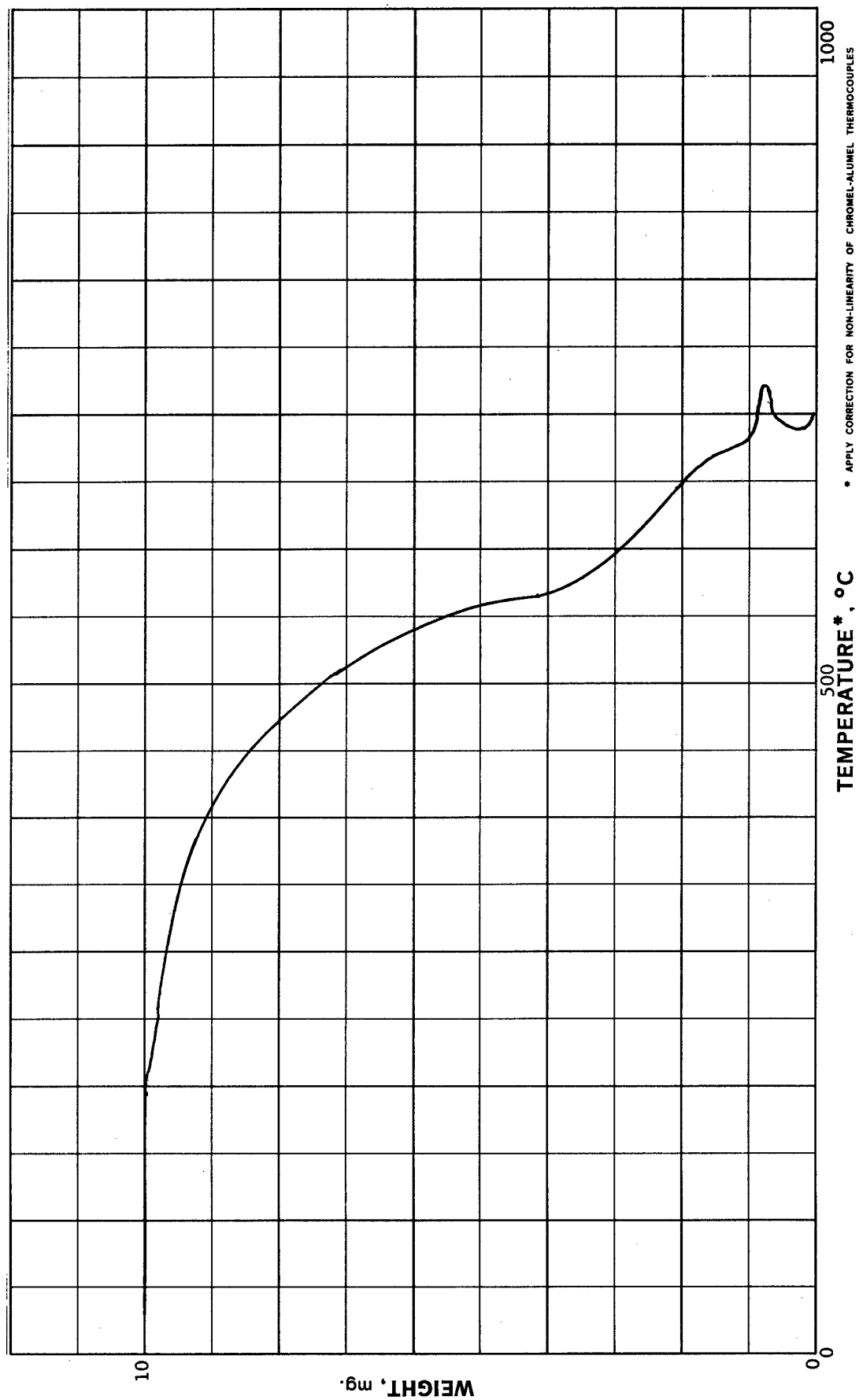
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 29. TGA in Air of BTEP-8 + 5% w/w Bz₃N (H225.

53

Figure 30. TGA in Air of BTEP-9 + PDA (1:1 mole) H250.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE*, °C

WEIGHT, mg.
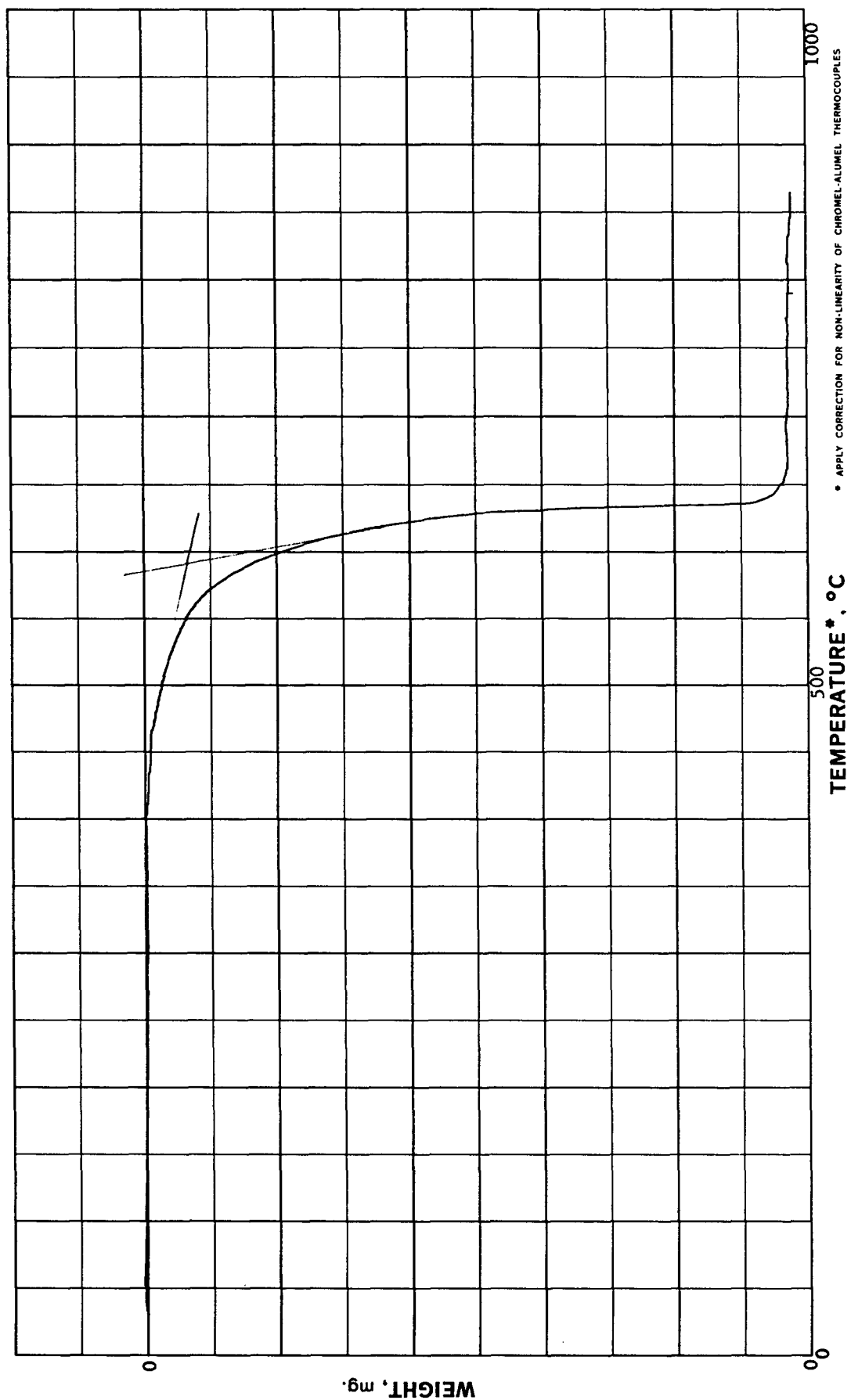
Figure 31. TGA in Air of BTEP-9 + 5% w/w Bz₃N (H250

55

WEIGHT, mg.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 32.   TGA in Air of BTSO-2.

Figure 33. TGA in Air of BTSO-2 Cured with 5% w/w Bz₃N H-225.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

TEMPERATURE*, °C

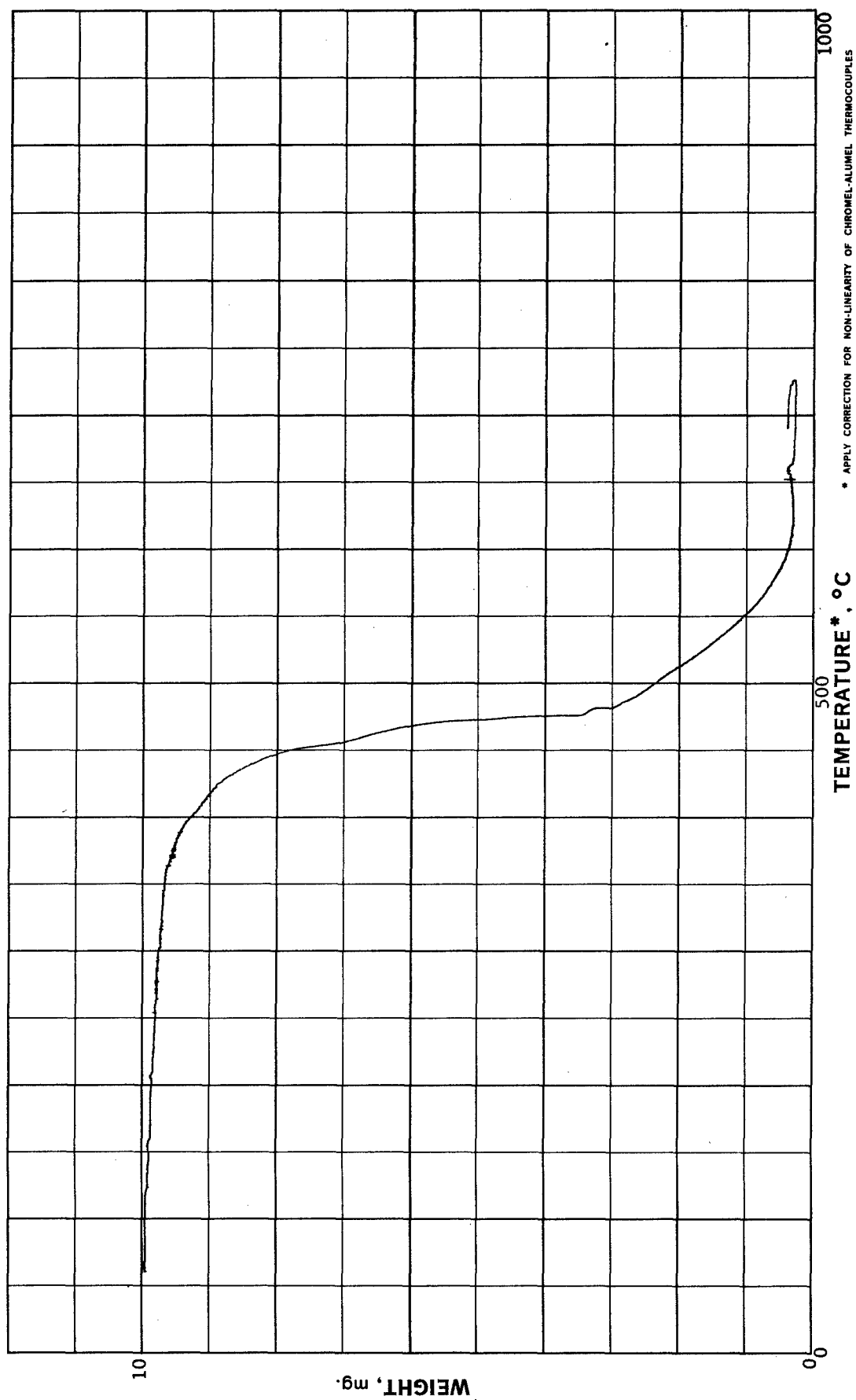Figure 34.   TGA in Air of BTSO-2 Cured with 1:1 mole m-PDA H-225.

58
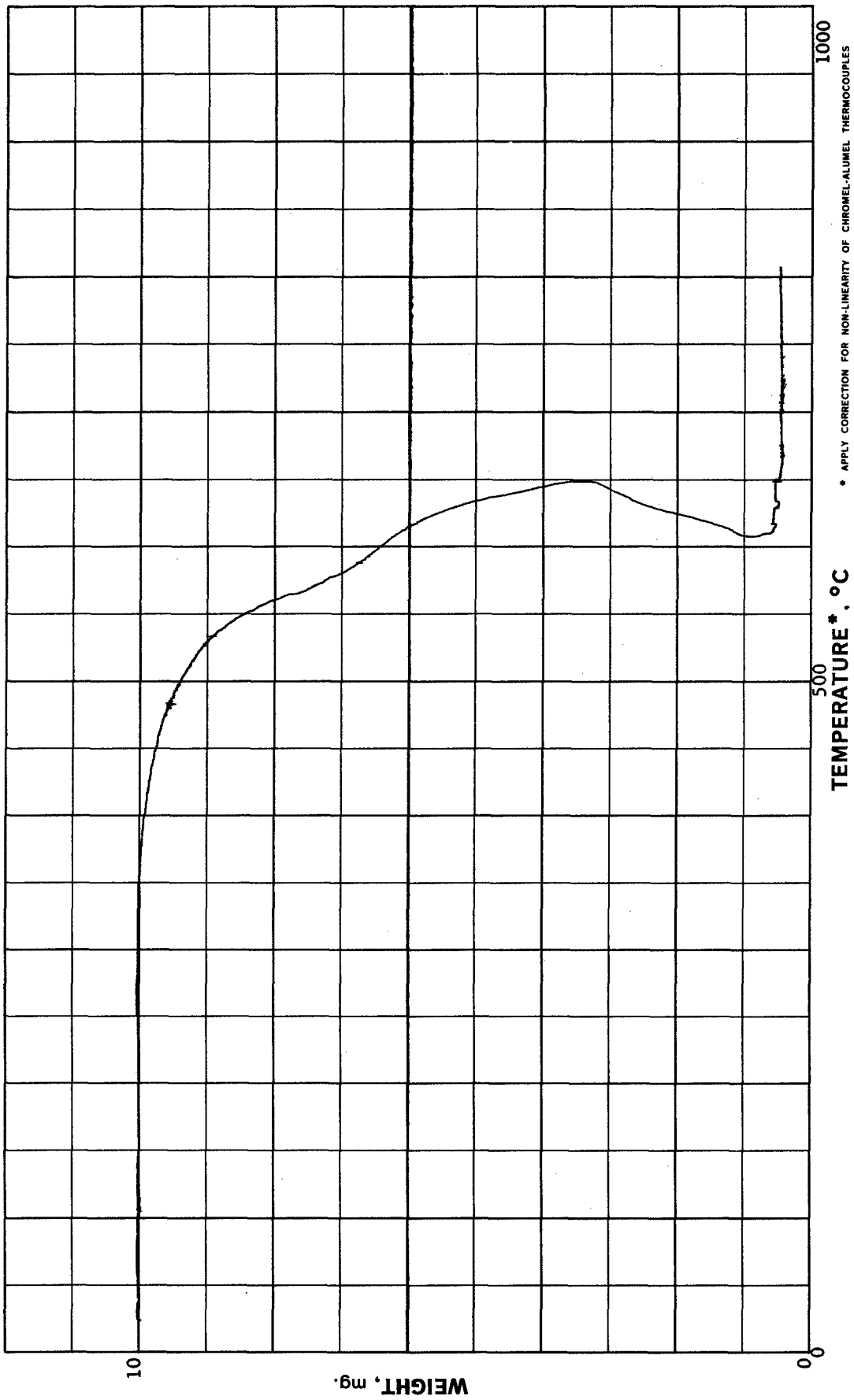
Figure 35.   TGA in Air of BTPN-1 Cured with Copper Metal.
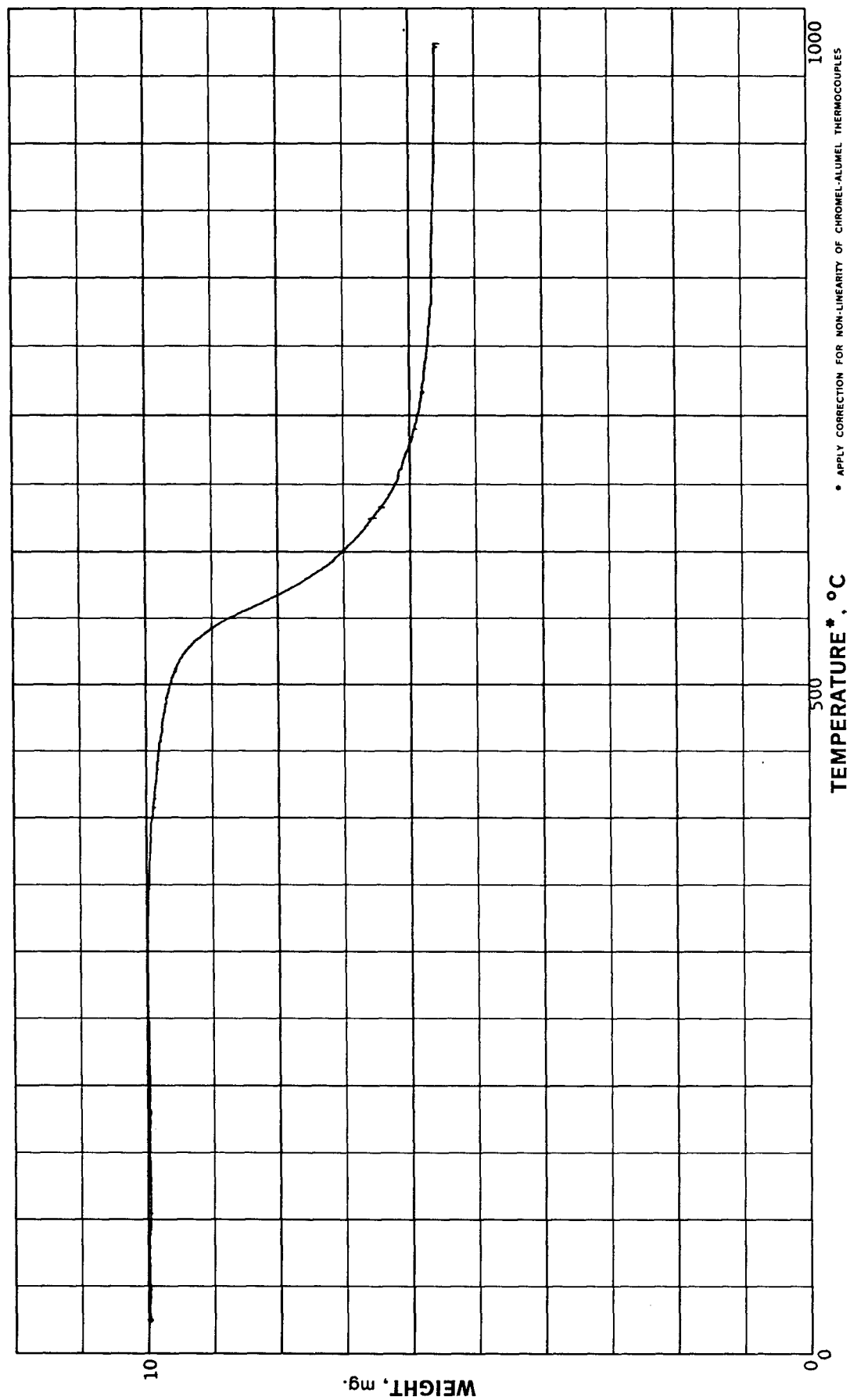
Figure 36. TGA in Nitrogen of BTPN-1 Cured with Copper Metal.

TEMPERATURE*, °C   * APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

60

Figure 37. TGA in Air of BTPN-1 Cured with Cu_2Cl_2.

61
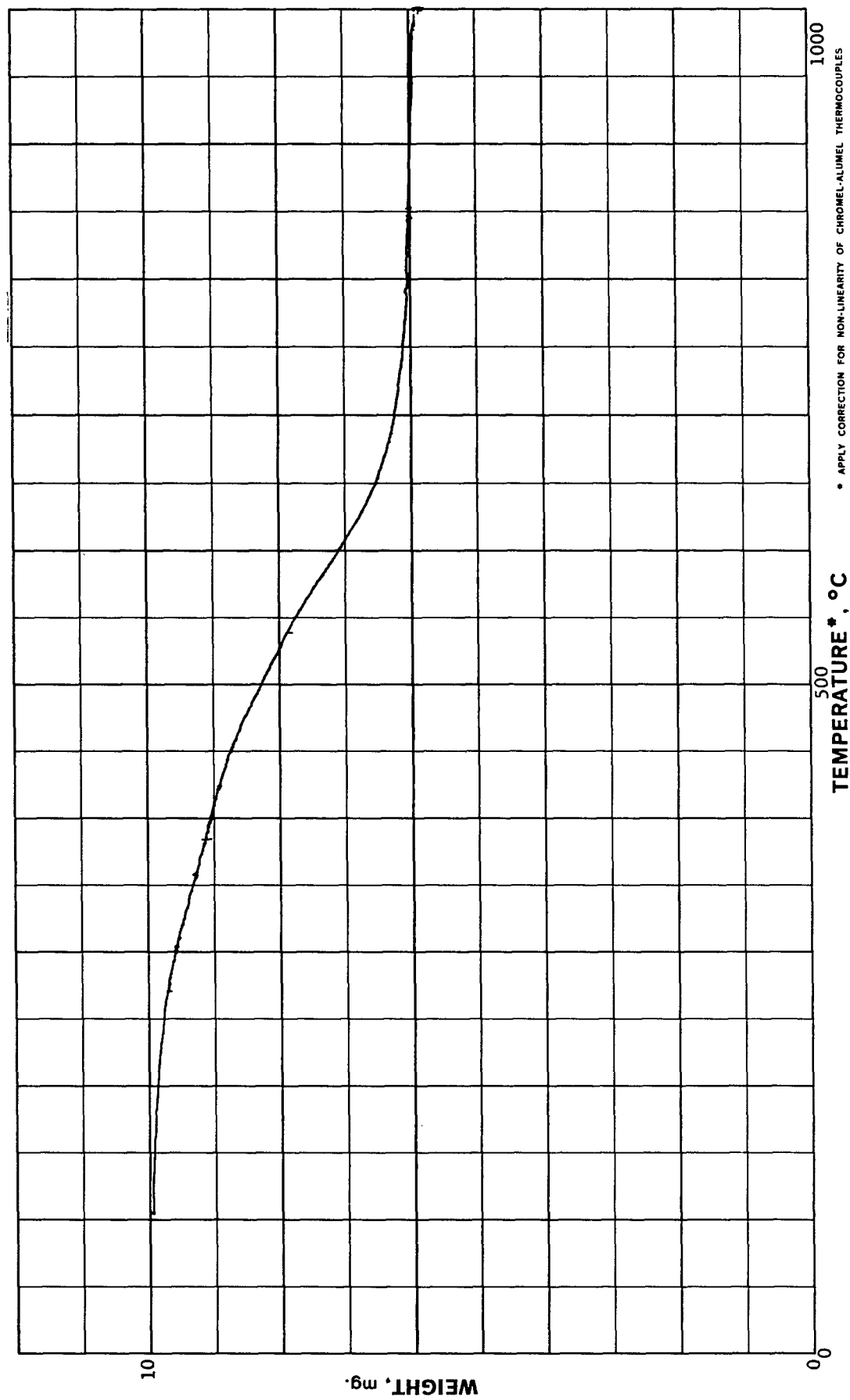
Figure 38.   TGA in Nitrogen of BTPN-1 Cured with Cu_2Cl_2.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE*, °C

WEIGHT, mg.
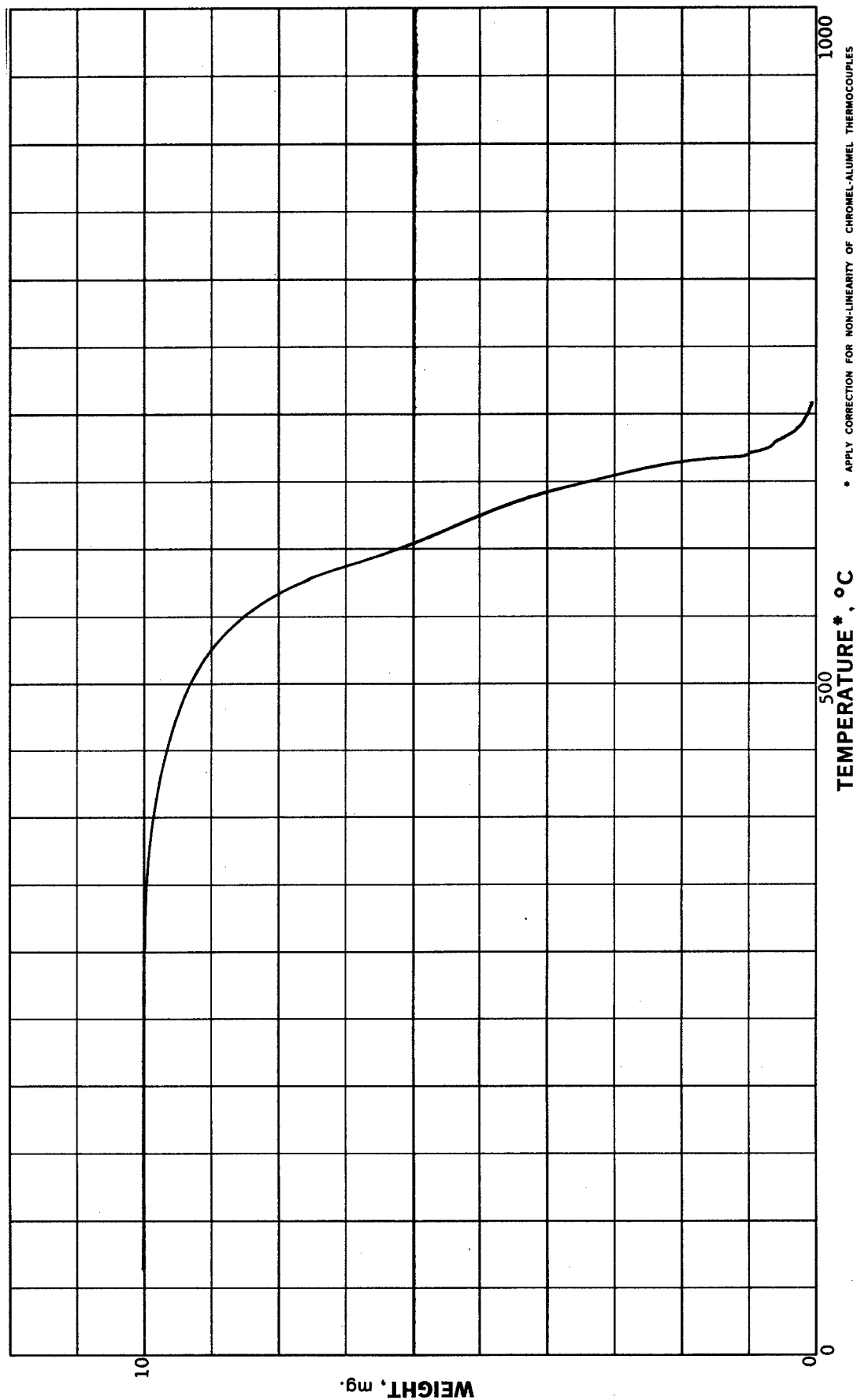
Figure 39.   TGA in Air of BTAS-16-H250.

TEMPERATURE*, °C   * APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
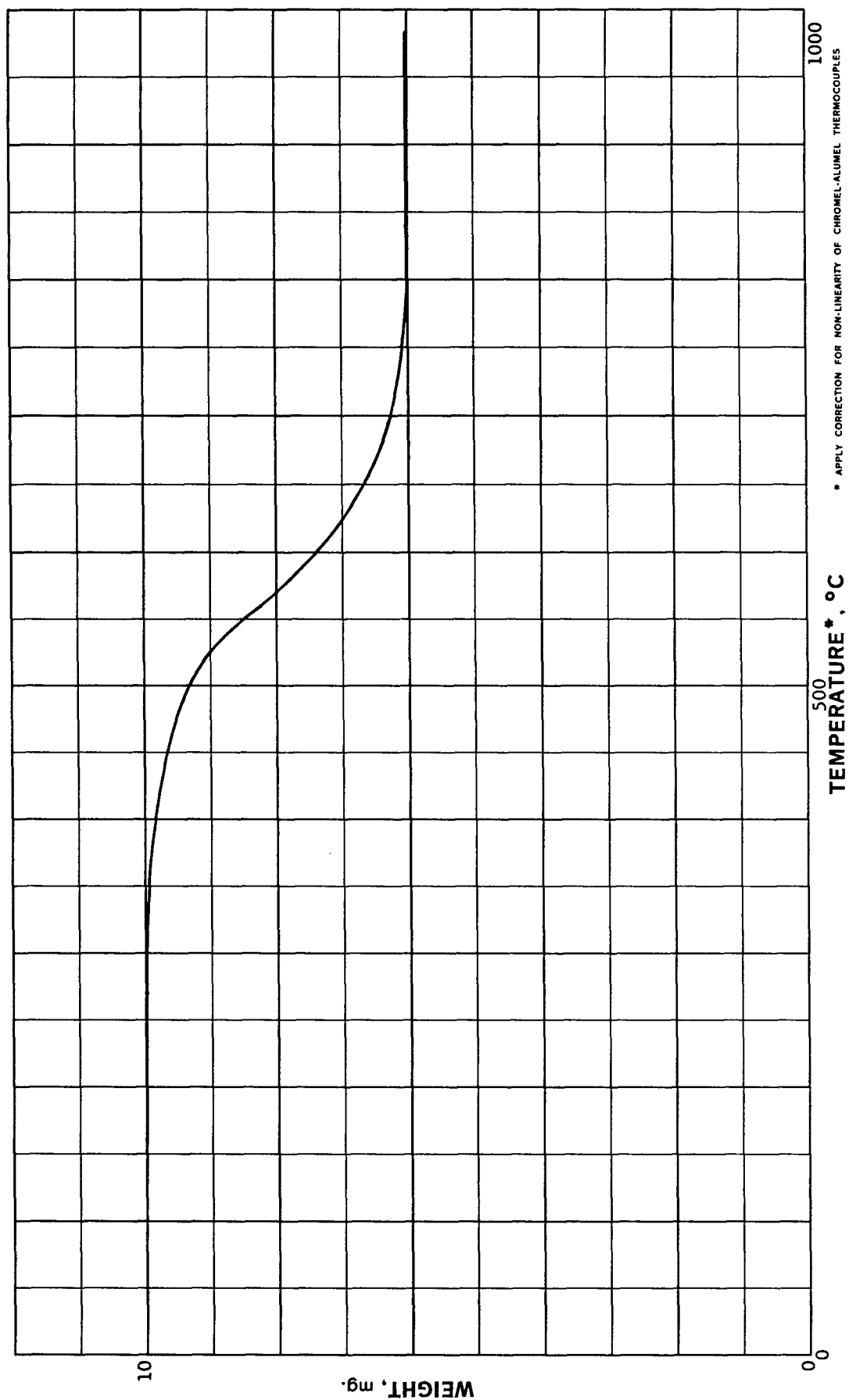
Figure 40.   TGA in Nitrogen of BTAS-16-H250.

Figure 41. TGA in Air of PI-25A.
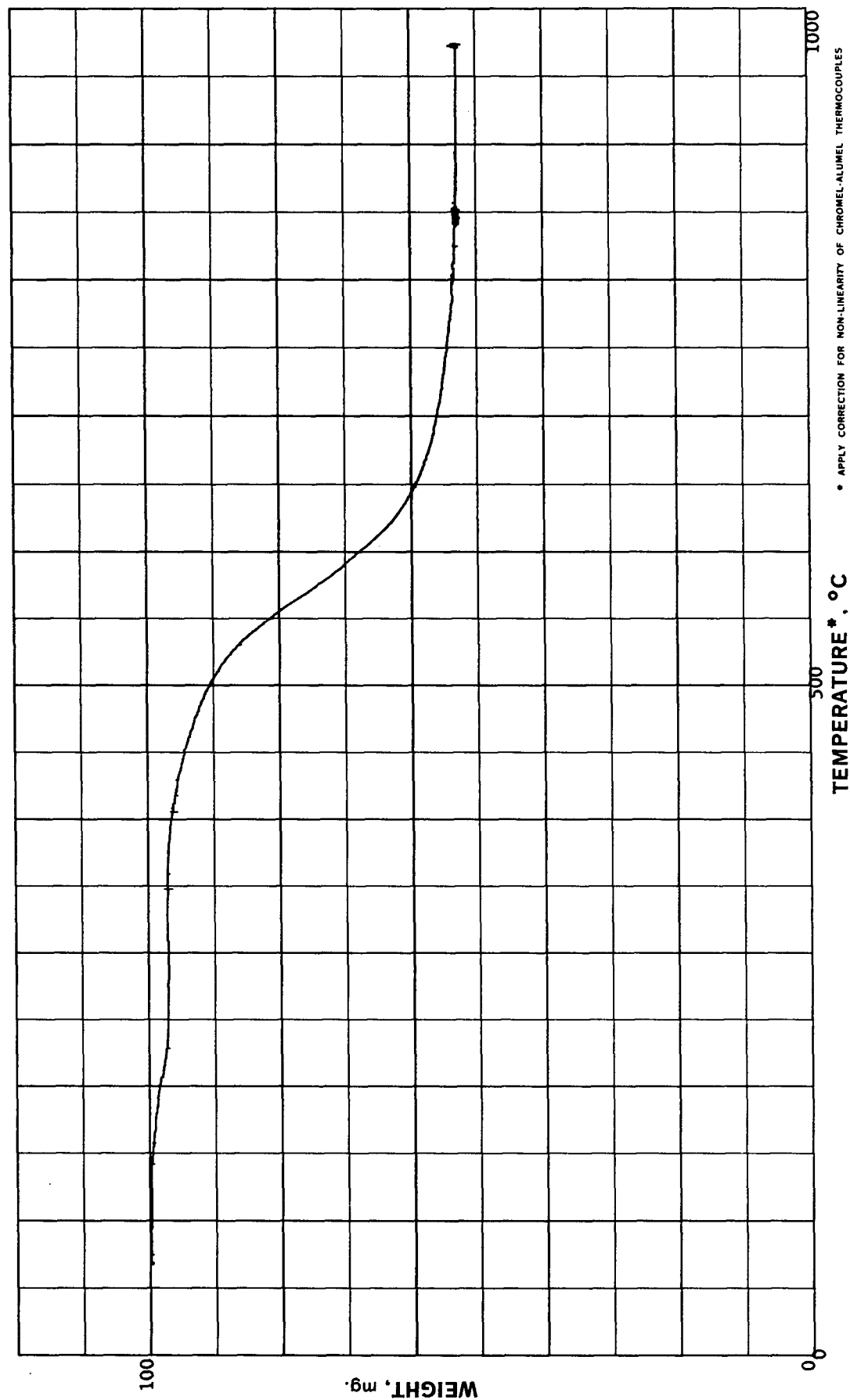
Figure 42. TGA in Nitrogen of PI-25A.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

TEMPERATURE*, °C

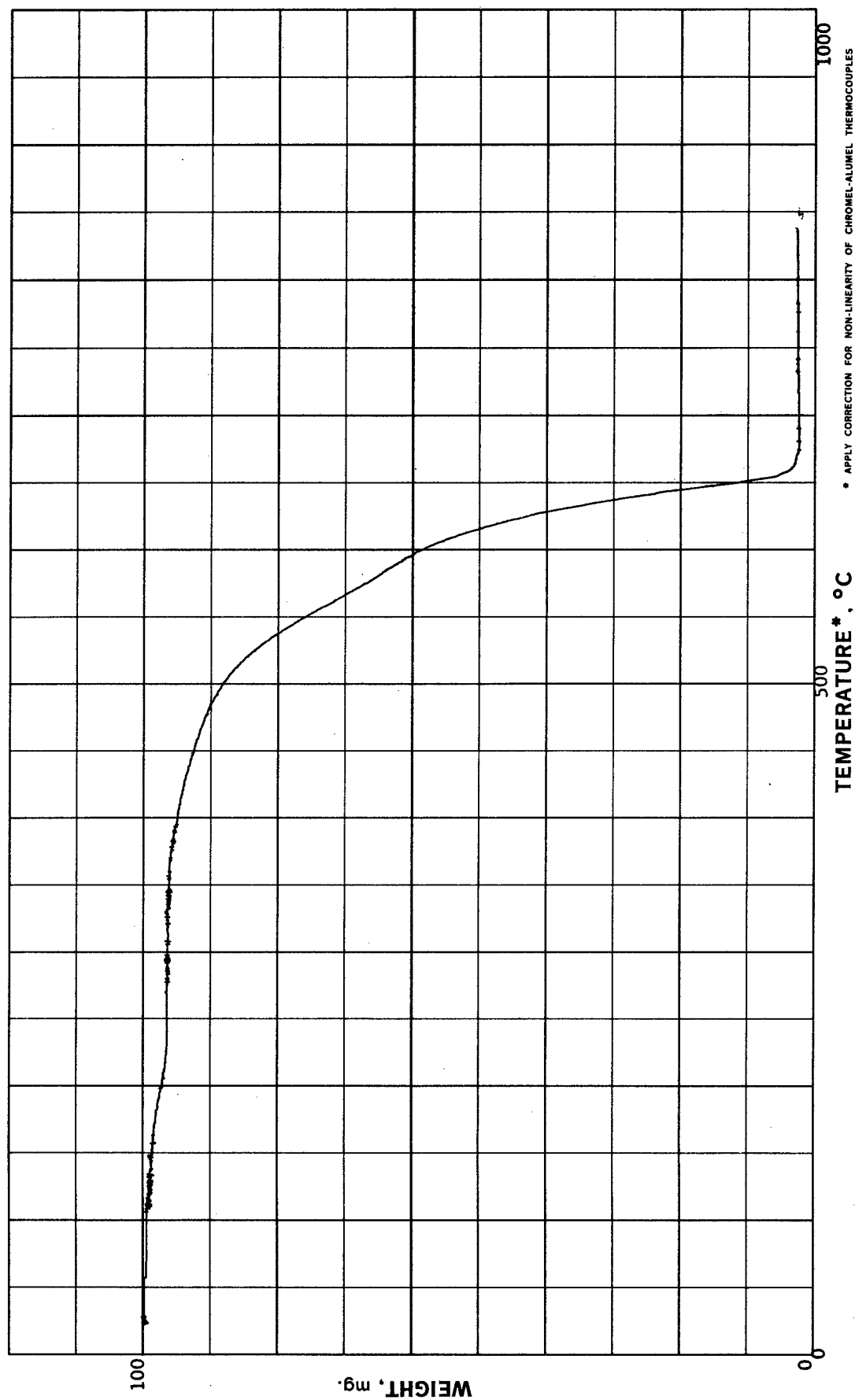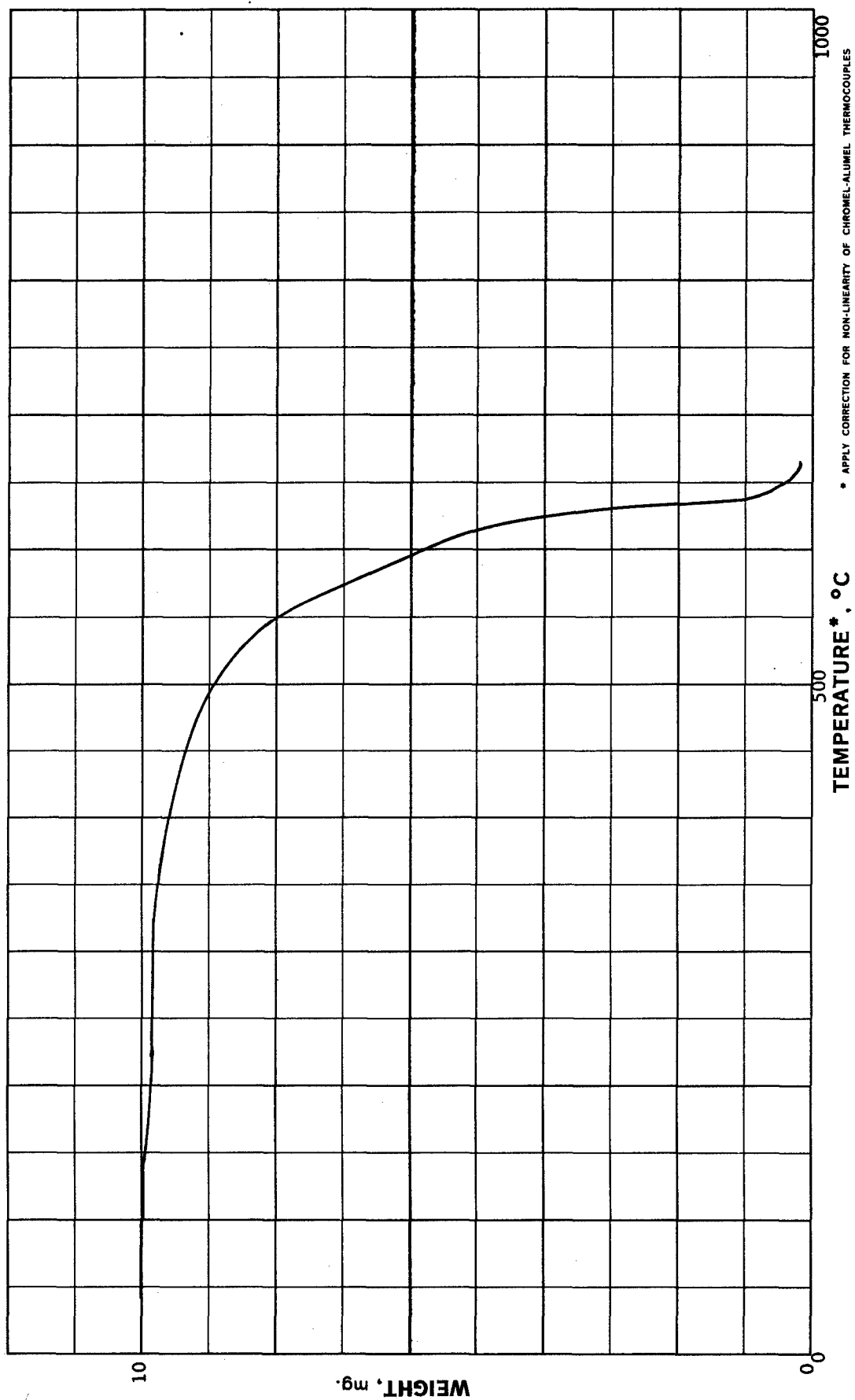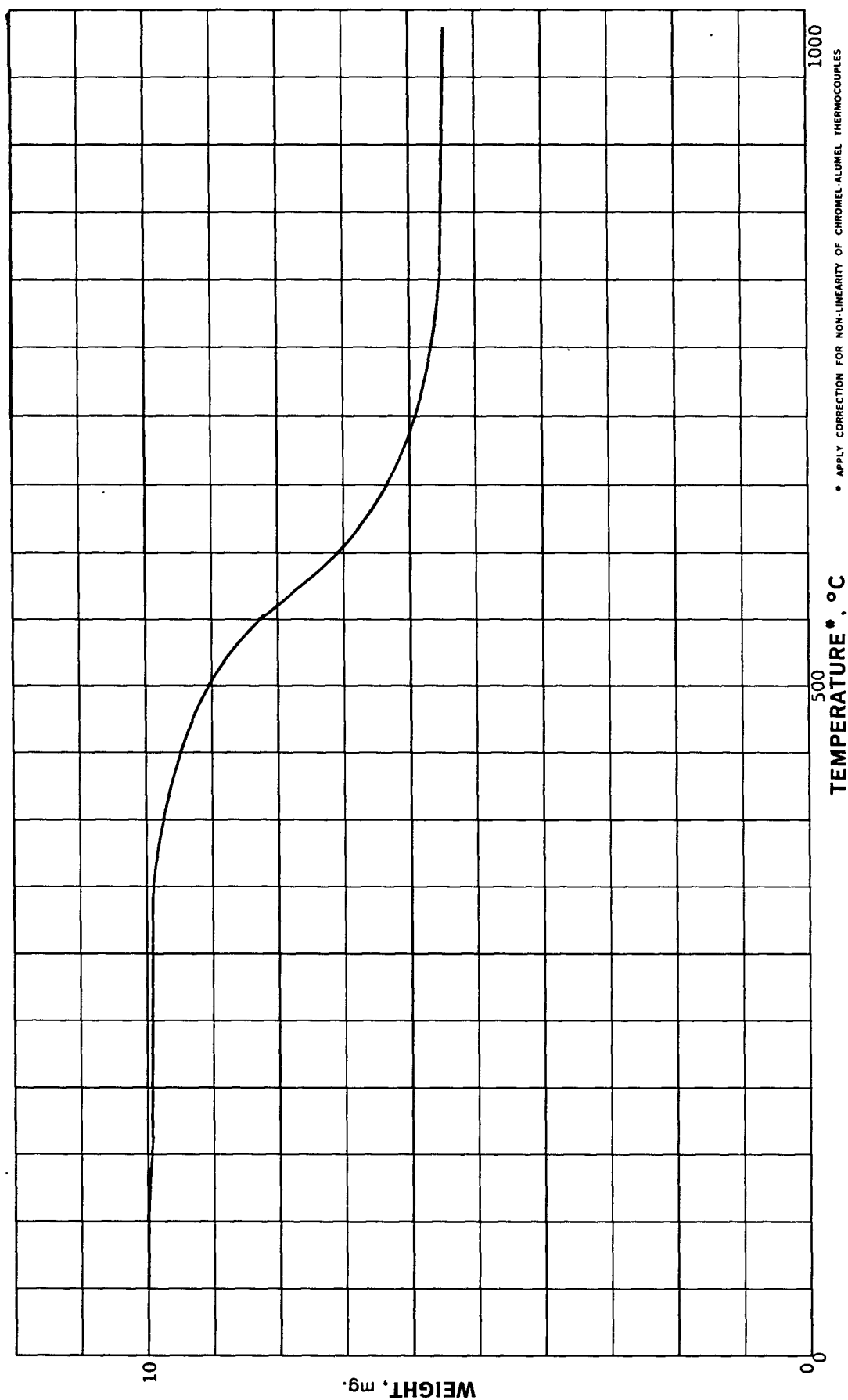* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

WEIGHT, mg.

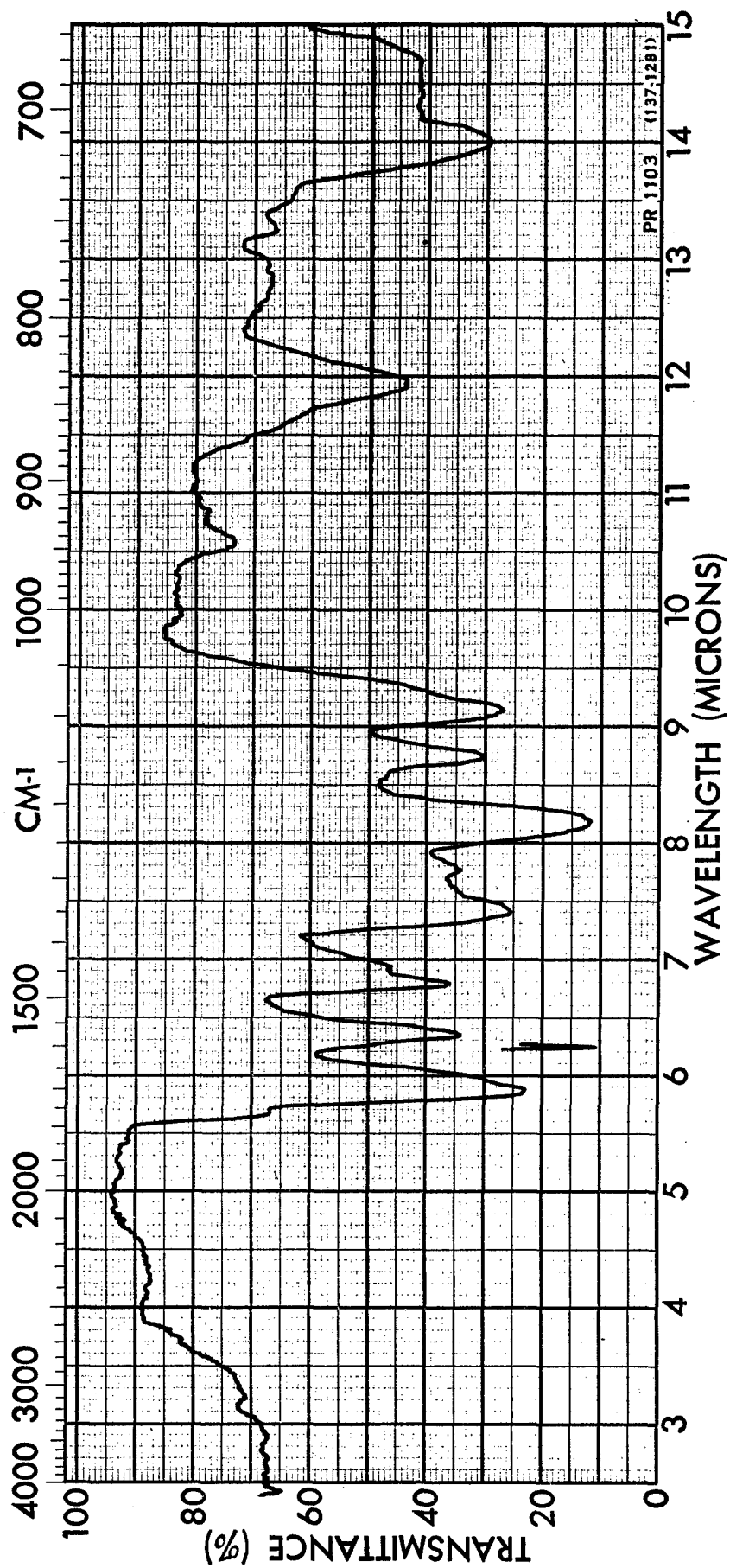Figure 43. TGA in Air of PI-25B.

Figure 44.   TGA in Nitrogen of PI-25B.

Figure 45.   Infrared Spectrum of PI-25B (KBr disc).

SECTION V

LIST OF ABBREVIATIONS AND SYMBOLS

APN	4-Aminophthalonitrile
AS	3-Aminostyrene .
BACS-4,3	Bis[4-(3-acetamidophenoxy)phenyl] Sulfone
BACS-4,4	Bis[4-(4-acetamidophenoxy)phenyl] Sulfone
BAPS-4,3	Bis[4-(3-aminophenoxy)phenyl] Sulfone
BNPS-4,3	Bis[4-(3-nitrophenoxy)phenyl] Sulfone
BNPS-4,4	Bis[4-(4-nitrophenoxy)phenyl] Sulfone
BTAS	Styrene-Terminated Oligomeric Polyimide
BTAT	Amine-Terminated Oligomeric Polyimide
BTCA	3,3',4,4'-Benzophenonetetracarboxylic Acid Dianhydride
BTEP	Epoxide-Terminated Oligomeric Polyimide
BTNP	Phthalonitrile-Terminated Oligomeric Polyimide
BTSO	Styrene Oxide-Terminated Oligomeric Polyimide
Bz_3N	Tribenzylamine
DAPB-3,3	1,3-Di(3-aminophenoxy)benzene
DAPB-3,4	1,3-Di(4-aminophenoxy)benzene
DMP-30	2,4,6-Tri-(dimethylaminomethyl)phenol
DNPB-3,4	1,3-Di(4-nitrophenoxy)benzene
EP	Epoxy Resin
EPC	Epichlorohydrin
m-PDA	meta-Phenylenediamine
NPA	4-Nitrophthalamide
NPI	4-Nitrophthalimide
NPN	4-Nitrophthalonitrile
ODA	4,4'-Oxydianiline
PI	Polyimide
SDA-3,3	3,3'-Sulfonyldianiline

SECTION VI

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18. Ibid., p. 66.